CRANFIELD UNIVERSITY

Ana Santos

MICROPOLLUTANTS REMOVAL AND TECHNOLOGICAL DEVELOPMENT OF MEMBRANE BIOREACTORS

School of Applied Sciences

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Supervisor: Professor Simon J. Judd

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ABSTRACT

The increasing worldwide contamination of aquatic environment with pollutants introduced by anthropogenic sources has become of great concern. Although present at low concentration, many of these pollutants have considerable long-term impacts on the ecosystem, such that extremely challenging legislative limits on their concentration in effluents are being proposed. This has led to the examination of membrane bioreactor (MBR) technology for wastewater treatment, since it offers the best and most consistent treated water quality of all biotreatment processes. However, both a review of the literature and experimental study reveals that MBRs appear to offer insufficient benefit over conventional processes to make their implementation for this duty viable, given their significantly higher cost. Notwithstanding this, the fate of micropollutants in MBR processes represents the most rapidly growing research topic in the general MBR subject area.

Despite the wide range of products commercially available, the majority are hollow fibre (HF) products based on polyvinylidene difluoride (PVDF) or polyethersulfone (PES) and almost all are in the pore size range between 0.04 and 0.4 μm. Whilst differences in module design across the whole range of products constrains their interchangeability, the increased acceptance of and confidence in this technology is reflected in the increased rate of implementation of large installations and the overall exponential growth in the market of 11-13% *per* year. However, there appears to be a dysfunction between the needs of the industry and the primary research area within the academic community, with practitioners identifying clogging as the main impediment to sustainable operation while 31% of all research papers published to end 2009 were based on fouling and less than 1% on clogging.

Experimental study of operation of an MBR to treat municipal wastewater based on a new HF material has revealed that studies based on aeration step provide a more realistic indication of critical operation than classical flux step experiments, since the latter involve imposing a hydraulic shock on the membrane. Simple measured sludge fouling propensity parameters did not appear to relate to fouling rate, with a counter-intuitive relationship arising under some operating conditions.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometry
A_m	Membrane Area
AS	Activated Sludge
ASP	Activated Sludge Plant
BOD	Biological Oxygen Demand
c.	Approximately
CAS	Conventional Activated Sludge
CASP	Conventional Activated Sludge Process
CEB	Chemically-Enhanced Backflush
cf.	Compare
Conc.	Concentration
COD	Chemical Oxygen Demand
CRM	Certified Reference Material
CST	Capillary Suction Time
d	Days

DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
EC	European Commission
EDC	Endocrine Disrupting Compounds
EDTA	Ethylenediaminetetraacetic acid
e.g.	For example
EQS	Environmental Quality Standards
et al.	And others
EPM	Extracellular Polymeric Materials
EPS	Extracellular Polymeric substances
EU	European Union
F	Footprint
FE	Final effluent
FS	Flat sheet
FST	Final Settlement Tank
GAC	Granular Activated Carbon
HF	Hollow fibre
HRT	Hydraulic Retention Time
hrs	Hours
i.e.	In other words
iMBR	Immersed membrane bioreactor
MBR	Membrane Bioreactor
MF	Microfiltration
MLD	Megalitres *per* day
MLSS	Mixed Liquor Suspended Solids
MT	Multitube
MLVSS	Mixed Liquor Volatile Suspended Solids
NTA	Nitrilotriacetic acid
NVSS	Non Volatile Suspended Solids
O&M	Operations and Maintenance
OEM	Original equipment suppliers
PAN	Polyacrylonitrile
PCM	Polycyclic Musk Fragrances

p.e.	Population equivalent
PE	Polyethylene
PES	Polyethersulfone
pH	-log $_{10}$[Hydrogen ions]
PP	Polypropylene
PPCP	Pharmaceuticals and Personal Care Products
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene difluoride
RAS	Return Activated Sludge
RO	Reverse Osmosis
s	Solubility
sBOD	Soluble Biological Oxygen Demand
sCOD	Soluble Chemical Oxygen Demand
SD	Standard Deviation
sec	Seconds
sMBR	Sidestream membrane bioreactor
SMP	Soluble Microbial Products
SRT	Sludge Retention Time
SS	Suspended solids
SVI	Sludge Volume Index
SSVI	Stirred Sludge Volume Index
TF	Trickling filter
TMP	Transmembrane pressure
TSS	Total suspended solids
Tu	Tubular
UF	Ultrafiltration
UK	United Kingdom
USA	United States of America
vs	Against
VSS	Volatile Suspended Solids
WFD	Water Framework Directive
WwTW	Wastewater Treatment Work

LIST OF NOTATIONS

ADBI	Celestolide
Ag	Silver
AHTN	Tonalide
Al	Aluminium
As	Arsenic
CBZ	Carbamazepine
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
DCF	Diclofenac
dTMP/dT	Fouling rate
DZP	Diazepam
Fe	Iron
g	Gravitational Acceleration
Hg	Mercury
HHCB	Galaxolide
IBP	Ibuprofen
J	Flux
J_c	Critical flux
K	Permeability
K_d	Sludge-water distribution coefficient
K_{oc}	Organic carbon-sorption partition coefficient
K_{ow}	Octanol-water partition coefficient
Mn	Manganese
M_w	Molecular weight
NH_3	Ammonia
NH_4^+-N	Ammoniacal nitrogen
NH_4^+	Ammonium
NO_x	Nitrogen oxide compounds
NPX	Naproxen

Ni	Nickel
NO_3	Nitrate
NO_3^+-N	Nitrate nitrogen
Pb	Lead
pH	-log $_{10}$[Hydrogen ions]
pK_d	-log $_{10}$[K_d]
ppb	Part *per* billion
ppt	Part *per* trillion
r^2	Coefficient of determination of a linear regression
SAD_m	Specific Aeration Demand
$SAD_{m,\ crit}$	Critical Specific Aeration Demand
V	Vanadium
Zn	Zinc
°C	Celsius
φ	Packing density
φ_{panel}	Panel packing density

1 INTRODUCTION

1.1 Micropollutants in the environment

Over the last decade-or-so, concern about micropollutants has grown with their increasing concentration in the environment and their impact on fauna and, potentially, humans. Most micropollutants are persistent, being only partially removed during wastewater treatment, and thus provide a significant pollution load when discharged into the environment over an extended period of time.

In October 2000, a new European directive, the Water Framework Directive 2000/60/EC (European Commission, 2000), came into force with the purpose of establishing a global framework for the protection of inland surface waters (rivers and lakes), transitional waters (estuaries), coastal waters and groundwater. By the end of 2015, all aquatic ecosystems and terrestrial ecosystems and wetlands must meet “good status”. Under this Directive, environmental quality standards (EQS) are set according to the risk imposed and impacts on the whole ecosystem and on human health. Standards are provided as threshold values below which no adverse impact is expected on either human health or the environment.

The arising impacts of metals on humans and aquatic environments have been of major concern since the early 1970s. Various metal compounds are natural components of the Earth’s crust and thus provide a background concentration, but it is the anthropogenic sources that are of primary concern since they elevate the naturally low concentrations to potentially harmful levels. Metals are ubiquitous in wastewater, entering the system *via* different routes (Sörme and Lagerkvist, 2002; Figure 1.1). Since they cannot be degraded, metals persist in the environment and tend to accumulate throughout the food chain as they are absorbed by living organisms. Although present in relatively small quantities, copper and zinc perform important physiological functions. However, when ingested beyond threshold concentrations they can cause acute or chronic

toxicity in higher organisms, microorganisms and plants (Chipasa, 2003; IOSHIC, 1999).

Metals removal by the conventional activated sludge process (CASP) has been extensively studied over the past 30 years, and the potential of membrane bioreactor (MBR) for removing micropollutants has also been studied and recently reviewed (Chapter 2). Although much work has been carried out on biomass removal efficiency for metals there is relatively little known on the metals adsorption by available biomass at the high sludge retention times and commensurately high solids concentrations prevailing in an MBR within a wastewater treatment plant.

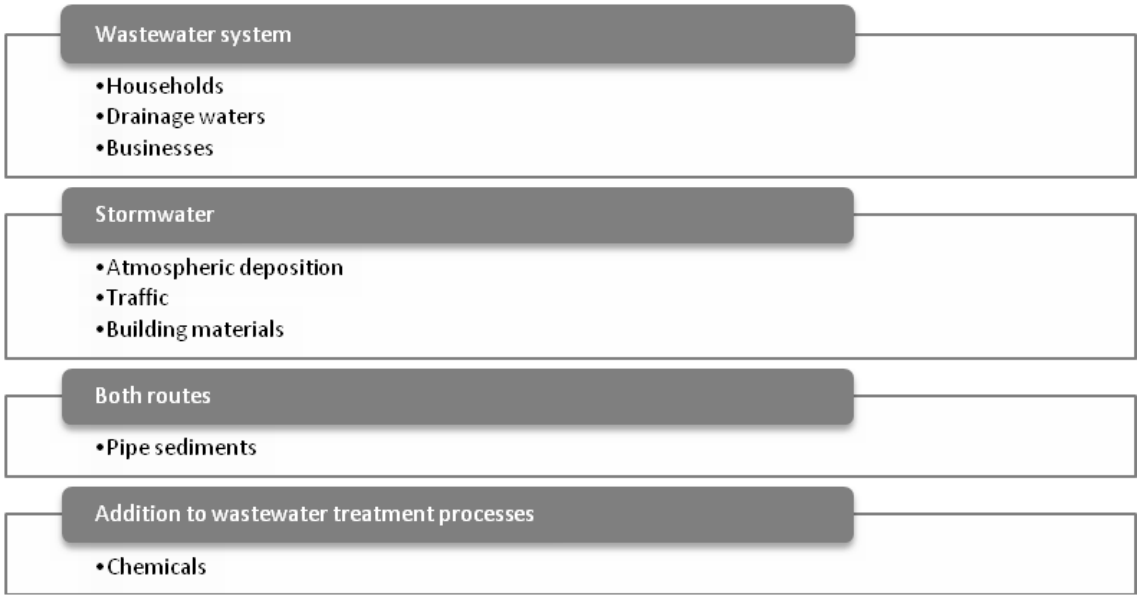

Figure 1.1 Sources of metals to wastewater (adapted from Sörme and Lagerkvist, 2002)

It is generally recognised that metals removal occurs during two stages of conventional wastewater treatment:

- Primary sedimentation: at this stage removal is largely physical, the insoluble metals fraction being removed by settlement of insoluble metal precipitates possibly coupled by adsorption onto the surface of the particulate material (Oliver and Cosgrove, 1974).

- Biological treatment: a proportion of the colloidal and dissolved fractions passing through the primary sedimentation stage are removed either by adsorption onto or absorption into the biomass flocs (Lester, 1987).

As well as metals, the impact of pesticide residues on watercourses and groundwater have become of increasing environmental concern, due to their adverse biocidal effects on non-target species. Permethrin is a synthetic pyrethroid insecticide widely used in agriculture, domestic, industrial and healthcare applications. Once in the aquatic environment in the μg l^{-1} range, permethrin can significantly affect the quality and quantity of insects and invertebrates (Cuppen *et al.*, 2000; Başer *et al.*, 2003; González-Doncel *et al.*, 2003). However, it is apparently relatively non-toxic to mammals (Rebach, 1999). Its removal by conventional wastewater treatment is largely dependent on the nature of the treatment process involved (Meakins *et al.*, 1994). Its non-polar and hydrophobic characteristics mean that permethrin tends to adsorb strongly onto soil and biota, or within a biological treatment process onto the wastewater sludge where it persists (Laskowski, 2002; Sharom and Solomon, 1981). This suggests that mechanical separation techniques, such as sedimentation, would significantly concentrate permethrin and similar organic micropollutants in the primary and secondary sludges of a wastewater treatment process (Meakins *et al.*, 1994). Compared with metals, very little has been published regarding the levels of permethrin in municipal wastewater, the mechanisms responsible for its removal, and the removal efficiency (Abram *et al.*, 1980; Plagellat, 2004; Kupper *et al.*, 2006; Gómez *et al.*, 2007).

1.2 MBR technology

Membrane bioreactor technology has been available for around 40 years, with the first sidestream technology commercialised by Dorr Oliver in the late 1960s (Bemberis *et al.*, 1971). However, only the last 20 years that has seen a rapid growth on its implementation and subsequent significant penetration of the municipal market, coinciding with the introduction of the immersed configuration (iMBR) (Judd and Judd, 2006; Yamamoto *et al.*, 1989). The MBR market value doubled in the five years between 2000 and 2005 to reach $217 and is expected to increase its market value from $296 million in 2008 to $488 million in 2013 (Hanft, 2008); growth at average rate of 11.6-12.7% *per annum* since the turn of the Millennium has been reported (Hanft, 2008; Srinivasan, 2007), the rate diminishing marginally towards 2013. However, even with the latter slowdown associated with the global financial crisis from 2008 onwards, the prospects for the technology appear favourable.

Technological innovation (*i.e.* the processes involved in development of a technology for introduction into the market place) generally is subject to drivers and barriers which ultimately determine the extent of implementation. It is widely recognised that a major driver for advancement of municipal water and wastewater treatment technology is legislation, setting limits for, amongst other things, discharge water quality and freshwater abstraction. Legislation is in turn driven by a number socioeconomic and other factors such as water scarcity and public perception, and ultimately has encouraged wastewater reuse for non-potable applications as a means of preserving freshwater sources. Reuse is particularly favoured in regions where ageing, or in many cases non-existent, infrastructure is in place to allow treatment by large centralised facilities, further propelling the MBR market (Atkinson and Menzefricke, 2006).

It is primarily in the area of water reuse, or applications demanding high treated effluent quality, where MBRs have met with success. MBRs combine conventional biotreatment with membrane separation either outside or inside the biotank. The membranes are normally either planar (hence flat sheet, FS) or

cylindrical (hence hollow fibre, HF) in shape if internally placed, or multi-tube (MT) if external. The most often-cited advantages offered by MBRs over CASPs are widely recognised, and of these the ones most often cited are (Judd, 2008):

- high quality, clarified and largely disinfected product water,
- small plant footprint
- high degree of process control with respect to residence times of the liquid and solids,
- favourable biological conditions for biotreatment, particularly for ammonia removal, and
- reduced waste solids (sludge) production.

Of these, it is the small footprint imparted and higher treated water quality which are usually of the most practical significance. An MBR replaces three unit operations in a conventional sewage treatment works: primary sedimentation, secondary biological treatment and tertiary filtration/disinfection. As a result, it is inherently simpler with respect to biotreatment process control.

However, MBR technology is subject to high capital and operating costs, as well as the negative perception associated with a relatively new technology (Frost & Sullivan, 2003) notwithstanding the fact that the immersed configuration is now 20 years old. In emerging regions such as Asia and Latin America, the lack of governmental support and limited availability of funds is restraining the expansion of MBR market, and is largely promoted through joint ventures and strategic partnerships with local vendors (Atkinson and Menzefricke, 2006).

The scope of research associated with such development would generally be expected to be determined by industrial or practitioner needs, as they relate to the specific technology (Chapter 4). For wastewater treatment technologies generally, these comprise largely generic qualities such as performance (with respect to product water quality), operational simplicity and robustness, capital

and operation and maintenance costs (O&M), with costs pertaining mainly to membrane replacement and energy demand (Judd, 2008; Verrecht *et al.*, 2010). In the case of MBRs, in common with all membrane technologies, a key process facet is that of membrane fouling.

Fouling is an inherent in membrane processes *per se*, arising from either deposition of material on the membrane surface to form a relatively impermeable layer or else occluding of the membrane pores (pore plugging). Both these phenomena tend to increase the resistance of the membrane to flow (*i.e*. reduce its permeability) and thus reduce process efficiency, manifested as an increased energy demand. Fouling has thus formed the basis of much research. However, other more practical aspects of MBR process operation, such as clogging of the membrane channels by gross solids and cleaning of membranes using chemicals, have received rather less attention – possibly contrary to the needs of practitioners (Chapter 4). This is possible because the academic community has tended to focus on maintaining membrane permeability through potentially controlling foulant generation, rather than through engineering of the process.

Fouling, clogging and cleaning all pertain to the maintenance of membrane permeability, and this is primarily sustained through membrane aeration. Aeration is a major parameter for both the hydraulic and biological process components; it maintains solids in suspension, provides oxygen to the biomass and scours the membrane surface. Energy demand and membrane replacement are the two most significant contributors to operating costs (Verrecht *et al.*, 2010; Kennedy and Churchouse, 2005), with aeration demanding between 10 and 50% of the total energy requirement (Verrecht *et al.*, 2010; Garcés *et al.*, 2007; Stone and Livingston, 2008). The efficacy of aeration is dependent on a number of system design facets, which include the membrane module design and the aeration mode, as well as the various operation and maintenance parameters. However, there appears to be little diversity in commercial designs with respect to membrane module dimensions (Chapter 3).

1.3 MBR technology and micropollutants

The efficacy of membrane bioreactors (MBRs) with respect to permeate quality is generally governed by the key universally regulated water quality determinants of biochemical (and sometimes chemical) oxygen demand, suspended solids and ammonia. Nutrient concentration is of increasing significance and in some circumstances the bacteriological content may be regulated. It is generally accepted that MBRs provide excellent treated water quality, achieving generally 4-6 fold removal of pathogenic bacteria, almost complete removal of suspended solids, and often reducing ammonia or TKN levels to less than 1 mg l^{-1} (Judd and Judd, 2010). It therefore stands to reason that only (a) onerous particles significantly smaller than the effective membrane pore size, and (b) non-biodegradable dissolved materials present a challenge to the process. Given that some viruses are comparable in size to that of the pore size of some MBR membranes it is possible that these may not be significantly rejected by the more porous MBR membranes, though in practice this does not seem to be the case (Hirani *et al.*, 2010). The challenge offered by non-biodegradable dissolved materials, such as typically exist in landfill leachate (Alvarez-Vazquez *et al.*, 2004) or industrial effluents such as petrochemical, dyeing and tannery wastewater (Fan *et al.*, 2000; Llop *et al.*, 2009; Qin *et al.*, 2007; Marrot *et al.*, 2004; Munz *et al.*, 2009) as well as the more recalcitrant micropollutants-bearing wastewaters, applies to all biotreatment and clarification processes. Removal of such materials by the process is dependent entirely on (a) their affinity for the sludge solids, and (b) the perm-selectivity of the membrane.

The intensity of the MBR process, associated with the higher biomass concentrations at which they operate and afforded by the uncoupling of hydraulic and solids retention times, may be expected to permit greater retention of recalcitrant dissolved materials by virtue of adsorption onto the commensurately higher solids surface area. Biodegradation of these species, however, relies on the development of a bacterial community at these long SRTs – ostensibly slow-growing ones – which are capable of breaking down the

organics. There is conflicting evidence of the efficacy of extending the SRT in MBR operation. There is little evidence of any improvement in removal of pathogenic microorganisms, including viruses (Hirani *et al.*, 2010; Zhang *et al.*, 2008; DeCarolis *et al.*, 2009). This is unsurprising given that particle rejection is similarly unaffected by their concentration in the reactor. However, there is also contradictory information concerning soluble organic and inorganic micropollutants. Removal of the soluble species, which are not directly rejected by the membrane since they are orders of magnitude smaller than the membrane pore size, can either be through degradation or phase change. A change of phase may be either through volatilisation (assisted by aeration, *i.e*. sparging), adsorption onto solids or precipitation.

Metals represent an important group in the range of key soluble contaminants, the others being organic micropollutants, such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) generally, and nutrients, and specifically nitrate and phosphate, and their related compounds. Metals cannot be biodegraded but, as already stated, only assimilated into biomass or precipitated to expedite their removal (Fatone *et al.*, 2008). A recent review (Chapter 2) of available information from municipal wastewater treatment trials suggests that no significant removal of soluble (or dissolved) metals takes place in a bioreactor, such that any improved performance of an MBR over that of the CASP is associated entirely with rejection of metals present as solids.

It has been widely reported that complexation of some metals with organic ligands derived from extracellular polymeric substances is significant in determining their solubility (Guibaud *et al.*, 2005; Nakhla *et al.*, 2008). Metals which are largely complexed by soluble organic ligands may only be removed if these complexes dissociate to form species which have a higher affinity for the biomass (Lester, 1987). Therefore, metals with a stronger affinity for organic ligands, as reflected in higher log K values, would be expected to be less significantly removed. However, correlation of measured removal with literature log K values is poor (Chapter 6).

Unlike metals, organic micropollutants can potentially be biodegraded and, as such, some impact from solids and liquid retention time in the bioreactor may be expected for some of these species. A recent review of available literature for PPCPs (Sipma *et al.*, 2010) has revealed that:

- readily removed pharmaceuticals (acetaminophen, ibuprofen and paroxetine) are equally well removed in both ASPs and MBRs,
- for a few moderately removed species (sotalol and hydrochlorothiazide) and highly intractable species such as carbamazepine and some macrolides (Bernhard *et al.*, 2006; Göbel *et al.*, 2007), which are actually promoted by biotreatment through various physico-biochemical processes, there is no appreciable difference in performance between the ASP and the MBR,
- for many other PPCPs removal tends to be greater for the MBR, but not significantly so.

Some authors have reported little appreciable difference in the performance of an MBR over that of an ASP for removal of many pharmaceutical products (Clara *et al.*, 2004; Cirja *et al.*, 2008). However, significant improvements have been reported for poorly biodegradable persistent polar pollutants, such as diclofenac, mecoprop and sulfophenylcarboxylates (Bernhard *et al.*, 2006), chemically complex compounds such as ketoprofen and naproxen (Kimura *et al.*, 2005) and others such as the antidepressant fluoxetine (Radjenovic *et al.*, 2007; Radjenović *et al.*, 2009). This has been primarily attributed to the longer SRTs attainable by the MBR (Strenn *et al.*, 2004; Lesjean *et al.*, 2005; Clara *et al.*, 2005), and studies conducted at very long SRTs, and commensurately low F/M ratios, have yielded better removals for some species (Göbel *et al.*, 2007). Studies have shown similar removals for CASPs and MBRs for some species when both processes have been operated at the same SRT (Clara *et al.*, 2004). However, several investigators have found no clear correlation between SRT and biodegradation of pharmaceuticals (Zhang *et al.*, 2008; Lishman *et al.*, 2006; Vieno *et al.*, 2007), since for some compounds such as diclofenac and

17a-ethinylestradiole (Clara *et al.*, 2005) other operating parameters appear to be important; little additional removal is attained at SRTs greater than 30 days (Suárez *et al.*, 2008).

Other parameters have also been studied. Whilst both hydraulic residence time (HRT) and operating temperature may both be expected to impact on removal, there appears to be little evidence of this in practice. Even with the associated widely fluctuating loadings, the performance of decentralised plants has been shown to be similar to those of larger centralised systems (Abegglen *et al.*, 2009). Evidence suggests that degradation of some EDCs present at ng l^{-1} concentrations follows pseudo first-order kinetics (Joss *et al.*, 2006), such that their percentage removal is independent of concentration but highly dependent on residence time if the reactor configuration is plug flow. This appears to have been corroborated to some extent by studies of several acidic pharmaceuticals at a decreased pH (Urase *et al.*, 2005). pH is thought to influence removal according to the micropollutant pK_a value, the acid dissociation constant, since this would then affect its affinity for the largely hydrophobic sludge solids (Cirja *et al.*, 2008). An interesting correlation has been reported between pharmaceuticals removal and nitrification (Batt *et al.*, 2006; Pérez *et al.*, 2005); nitrifying bacteria, and enzymes such as ammonium monooxygenase specifically (Berthe-Corti and Fetzner, 2002), have been postulated as being capable of co-metabolising a wide-range of refractory organic micropollutants. There is also evidence of impacts of the presence or depletion of C and N (Drillia *et al.*, 2005) and oxygen (Zwiener and Frimmel, 2003), with significantly greater degradation of diclofenac demonstrated under anoxic than aerobic conditions.

There is evidently a need to understand both:(a) the fate of metals and organic micropollutants in municipal wastewater biological processes, (b) the extent to which MBRs offer an improvement in removal, and (c) the means by which the energy efficiency and overall cost of the MBR technology can be improved. The latter demands a systematic experimental appraisal of the impact of membrane characteristics on performance coupled with a review of the existing commercial

technologies and possible implications regarding costs, whilst metals fate and improvement in metals retention provided by the MBR can be appraised both experimentally and through a survey of the available literature.

1.4 Current study background and objectives

The practical work described in this thesis arose as a result of two studies, the first performed for a UK water utility in the North West of England and the second for a large US-based chemical company.

The water utility initiated the project in response to the Water Framework Directive and the highly challenging water quality specifications with specific regard to copper, zinc and the pesticide permethrin. The project, forming part of the company's "Dangerous Substances" programme, aimed to establish the most optimum performance of the existing wastewater treatment assets with respect to the removal of these target micropollutants, and assess the possible benefits offered by membrane technology. One of the premises of the programme was that micropollutant levels generally, and metals specifically, would be at their highest in the return liquors from sludge processing operations, also high in settleable solids, and that the selective treatment of these streams would therefore be more efficient than treating the complete flow. A second premise was that increased removal efficiency would be provided both at highest mixed liquor concentrations, where the total adsorptive surface area would also be at its highest. Lastly, it was expected that the use of a membrane for complete solids retention would provide the greatest removal.

The second component of the experimental study concerned the evaluation of a specific hollow fibre (HF) membrane material as a membrane bioreactor technology. This study aimed to establish optimum performance in terms of the membrane fouling rate under different membrane aeration regimes, and assess the impact of different membrane modules.

Accordingly, the specific objectives for the programme are as follows, with the corresponding thesis section identified. The objectives were addressed through the completion of six papers (Table 1.1), all of which were co-authored and all submitted to peer-reviewed journals, with the exception of Chapter 9, and for which the inter-relationship between the outputs is indicated in Figure 1.2.

1. **Assessment of the state of the art**

- Establishing the current knowledge of metals fate in conventional and membrane-based wastewater biotreatment processes through a review of the scientific and technical literature (Chapter 2)

    - Chapter 2: Published in Journal of Environmental Monitoring (2010) 12, 110-118: Ana Santos and Simon Judd, *The fate of metals in wastewater treated by the activated sludge process and membrane bioreactors: A brief review*.

- Appraisal of the status of commercially available membrane products for immersed membrane bioreactors (iMBR), with specific reference to the municipal wastewater market (Chapter 3).

    - Chapter 3: Published in Separation Science and Technology (2010) 45, 850-857: Ana Santos and Simon Judd, *The commercial status of membrane bioreactors for municipal wastewater*.

- Appraisal of (a) the status of academic research in MBR technology, (b) the practitioner needs, and (c) the commercial membrane product specifications (with respect to their physical dimensions and so interchangeability), so as to provide an appreciation of the status of MBRs from the broadest possible perspective (Chapter 4).

    - Chapter 4: Published in Desalination (2010): Ana Santos, Wenjing Ma, Simon J. Judd, *Membrane bioreactor technology: two decades of research and implementation*, in press.

A version of Chapter 3 and 4 has been presented at a conference: Proceedings of the 9th Conference on Membranes in Drinking and Industrial Water Treatment, Trondheim Norway; Santos, A., Ma, W. and Judd, S. (2010): *MBR technologies: What have we got?*

2. Technical investigation

- Evaluation of fate and behaviour of Cu, Zn (Chapter 5) and permethrin (Chapter 7) and their removal using a pilot-plant installed at an existing full-scale WwTW for different steady-state operating conditions under appropriate conditions.

- Evaluation of the impact on Cu and Zn final effluent concentrations of replacing the secondary sedimentation tank with membrane filtration using a pilot-plant installed at an existing full-scale WwTW (Chapter 5 and 6).

    - Chapter 5: Published in Environmental Technology (2010) 31 (7), 725-743: Ana Santos, Paul Barton, Elise Cartmell, Frederic Coulon, Richard S. Crane, Peter Hillis, John N. Lester, Tom Stephenson and Simon J. Judd*, Fate and behaviour of copper and zinc in secondary biological wastewater treatment processes: II Removal at varying sludge age.*

    - Chapter 7: Published in Environmental Technology (2010): Ana Santos, Rubén Reif, Peter Hillis and Simon Judd, *Fate and behaviour of permethrin during conventional activated sludge treatment*, in press.

To supplement chapter 2 and chapter 5, a corollary about metal speciation (Chapter 6) has been added. The evaluation of six metals removal (cadmium, chromium, copper, lead, nickel and zinc) using a larger scale and close to representative MBR operational conditions is also addressed in this chapter.

- Evaluation of the hydraulic performance of a novel hollow fibre membrane module with reference to (Chapter 8 and Chapter 9):
    - Critical flux under different operating conditions, aeration demands and aeration regimes;
    - Evaluating the critical specific aeration demand of the central element under constant flux operation for intermittent and continuous aeration regimes;
    - Comparison of fouling rate under intermittent and continuous aeration regimes;
    - Benchmark performance against existing commercial systems.
        - Chapter 8: Published in Separation Science and Technology (2010) 45, 956-961: Hèctor Monclús, Sebastian Zacharias, Ana Santos, Marc Pidou and Simon Judd, *Critical flux and aeration demand determination in a hollow fibre membrane bioreactor*.
        - Chapter 9: Ana Santos, Wenjing Ma, Irene Somoza, Hèctor Monclús, Peter Aerts and Simon Judd, *Criticality of flux and aeration on different hollow fibre membrane bioreactor and sludge quality impact*, unpublished (supplemented with Appendix C and D).

The author provided practical and/or intellectual input to all of these papers, although for two paper below the work was predominantly fulfilled by the primary author and therefore these papers have been annexed (Appendix A and B):

- Appendix A: Published in Environmental Technology (2010) 31(7), 705-723: Crane, R.S., Barton, P., Cartmell, E., Coulon, F., Hillis, P., Judd, S.J., Santos, A., Stephenson, T. and Lester, J.N, *Fate and behaviour of copper and zinc in secondary biological wastewater treatment processes: I Evaluation of biomass adsorption capacity.*

- Appendix B: Published in Journal of Environmental Monitoring (2010): Rubén Reif, Ana Santos, Simon J. Judd, Juan M. Lema and Francisco Omil, *Occurrence and fate of Pharmaceutical and Personal Care Products in a sewage treatment works,* in press.

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Table 1.1 Thesis summary with input from author

Chapter	Publication	Practical input	Intellectual input
1	Introduction	✓	✓
2	Journal of Environmental Monitoring (2010) 12, 110-118: Ana Santos and Simon J. Judd, *The fate of metals in wastewater treated by the activated sludge process and membrane bioreactors: A brief review.*	✓	✓
3	Separation Science and Technology (2010) 45, 850–857: Ana Santos and Simon J. Judd*, The commercial status of membrane bioreactors for municipal wastewater.*	✓	✓
4	Desalination (2010): Ana Santos, Wenjing Ma and Simon J. Judd*, Membrane bioreactor technology: two decades of research and implementation,* submitted.	✓	✓
5	Environmental Technology (2010) 31 (7), 725-743: Ana Santos, Paul Barton, Elise Cartmell, Frederic Coulon, Richard S. Crane, Peter Hillis, John N. Lester, Tom Stephenson and Simon J. Judd, *Fate and behaviour of copper and zinc in secondary biological wastewater treatment processes: II Removal at varying sludge age.*	✓	✓
6	Ana Santos and Simon J. Judd: *Metal speciation*, unpublished.		✓
7	Environmental Technology (2010): Ana Santos, Rubén Reif, Peter Hillis and Simon J. Judd, *Fate and behaviour of permethrin during conventional activated sludge treatment,* submitted.	✓	✓
8	Separation Science and Technology (2010) 45, 956-961: Hèctor Monclús, Sebastian Zacharias, Ana Santos, Marc Pidou and Simon J. Judd, *Critical flux and aeration demand determination in a hollow fibre membrane bioreactor.*		✓
9	Ana Santos, Wenjing Ma, Irene Somoza, Hèctor Monclús, Peter Aerts and Simon J. Judd, *Criticality of flux and aeration on different hollow fibre membrane bioreactor and sludge quality impact*, unpublished.	✓	✓
10	Conclusions and suggestions for further work.		✓
Appendix A	Journal of Environmental Monitoring (2010): Rubén Reif, Ana Santos, Simon J. Judd, Juan M. Lema and Francisco Omil, *Occurrence and fate of Pharmaceutical and Personal Care Products in a sewage treatment works.*	✓	
Appendix B	Environmental Technology (2010) 31(7), 705-723: Richard S. Crane, Paul Barton, Elise Cartmell, Frederic Coulon, Peter Hillis, Simon J. Judd, Ana Santos, Tom Stephenson and John N. Lester, *Fate and behaviour of copper and zinc in secondary biological wastewater treatment processes: I Evaluation of biomass adsorption capacity.*	✓	
Appendix C	Ana Santos and Simon J. Judd: *Criticality of flux and aeration on different hollow fibre sidestream membrane bioreactor*, unpublished.	✓	✓
Appendix D	Ana Santos and Simon J. Judd: *Statistical analysis*, unpublished.	✓	✓

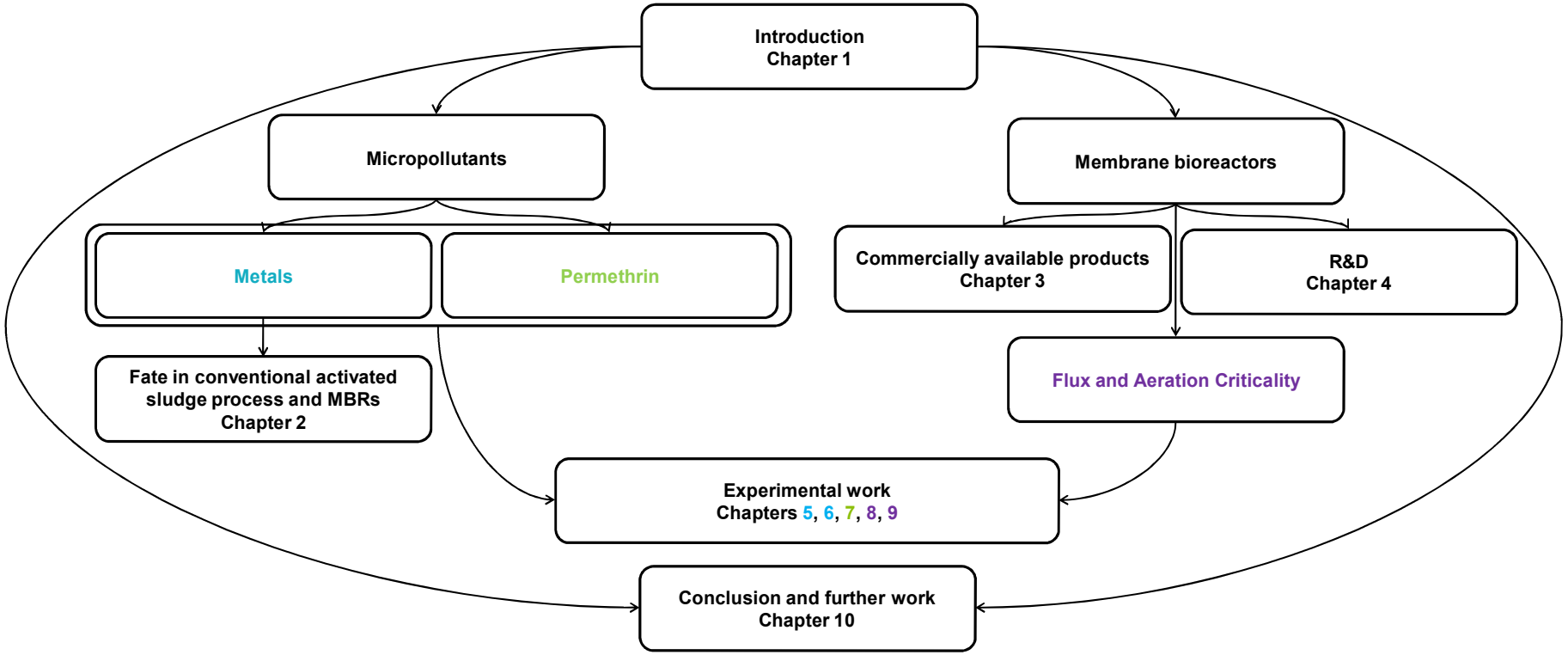

Figure 1.2 Thesis road map

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2 THE FATE OF METALS IN WASTEWATER TREATED BY THE ACTIVATED SLUDGE PROCESS AND MEMBRANE BIOREACTORS: A BRIEF REVIEW

Ana Santos and Simon J. Judd

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Centre for Water Science, Cranfield University, Bedfordshire, UK

Abstract

The fate of metals in wastewater treatment by the conventional activated sludge process (ASP) and membrane bioreactors (MBRs) is reviewed. The review outlines the environmental and health impacts of metals, but focuses primarily on data reported for removal of toxic metals, and some other high-profile inorganic micropollutants such as aluminium and arsenic, by wastewater treatment processes. Information from pilot and full-scale plants is included, with corroboratory reports from bench-scale tests. General trends in removal across different metals are considered, along with the impact of the key process operating determinant of solids retention time. It is concluded that the only consistent trend in metals removal is that it is most effectively achieved through efficient solids separation, and that this represents the primary advantage offered by the MBR. As such, MBRs achieve averaged metals removals which are consistently but not dramatically higher than the ranges reported by the ASP: 64-92% *vs* 46-87%, with no more than a 55% decrease on average in effluent concentration. The slightly greater removal attained is attributable to the additional suspended solids retention attained by the membrane process. In either case, further removal of metals would demand a tertiary process for removal of the dissolved material.

2.1 Metals in the environment

The arising and impacts of metals on humans and aquatic environments has been of major concern since early 1970s. Various metal compounds are natural components of the Earth's crust and thus provide a background concentration. However, it is the anthropogenic sources that are of primary concern, since they elevate the naturally low concentrations to potentially harmful levels. Since they cannot be degraded, metals persist in the environment and tend to accumulate throughout the food chain as they are absorbed by living organisms. In small quantities, some of these elements (*e.g.* chromium, copper, iron, manganese and zinc) perform important physiological functions. However, if ingested beyond threshold concentrations they can cause acute or chronic toxicity in higher organisms, microorganisms and plants (Chipasa, 2003), and it is this which has led to increasingly stringent legislation. Under the EU Water Framework Directive (2000/60/EC), environmental quality standards for metals are set according to the risk imposed and impacts on the whole ecosystem and on human health. Metals classified as potentially hazardous to the aquatic environment include cadmium, lead, mercury and nickel as priority substances (Annex X of the WFD), while copper, chromium and zinc are classified as potential main pollutants (Annex VIII) (European Commission, 2000). Standards are provided as threshold values below which no adverse impact is expected on either human health or the environment (Table 2.1).

Table 2.1 Existing UK environmental quality standards (EQS) to protect the most sensitive aquatic life (SEPA, 2004)

Substance	Environmental Quality Standards (EQS)						
	Freshwater, μg l^{-1}						Marine, μg l^{-1}
	List I						
Cd (tot.; diss.)	5						2.5
Hg (tot.; diss.)	1						0.3
	List II						
	Hardness, μg l^{-1} $CaCO_3$ [a]						
	0-50	>50-100	>100-150	>150-200	>200-250	>250	
Cr (diss.)	2	10	10	20	20	20	5
Cu (diss.)	0.5	3	3	3	8	12	5
Pb (diss.)	4	10	10	20	20	20	10
Ni (diss.)	8	20	20	40	40	40	15
Zn (diss.)	8	15	15	50	50	50	10

[a] These standards are related to the water hardness to take into account bioavailability of metals; Total: tot.; Dissolved: diss.

Much of the recent aquatic toxicology in particular, which has driven legislation in this area, has been concerned with the prediction of effects of pollutants with respect to effect of interaction between the different metals (Barata *et al.*, 2002; Chandra and Khuda-Bukhsh, 2004; Hansen *et al.*, 2002; Montvydiene and Marčiulioniene, 2004; Norwood *et al.*, 2003; Sindhe and Kulkarni, 2004), the significance and impact of environmental factors such as temperature, incoming solar radiation or other seasonal factors (Babu *et al.*, 2003; Ghosal and Kaviraj, 2002; Heugens *et al.*, 2003; Maraldo and Dahllöf, 2004; Rathore and Khangarot, 2002), and factors influencing the bioavailability of metals (De Schamphelaere *et al.*, 2004; Eggleton and Thomas, 2004; Janssen *et al.*, 2003; Luider *et al.*, 2004; Meylan *et al.*, 2004; Ravichandran, 2004). Recorded toxic effects include damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergic reactions are not uncommon, and repeated long-term contact with some metals or their compounds may even cause cancer (IOSHIC, 1999).

2.2 Metals in wastewater treatment

Toxic metals are almost ubiquitous in wastewater, arising from a diverse range of sources. In the past, industrial activities have always been a significant source of heavy metals (Lester *et al.*, 1979; Stoveland *et al.*, 1979; Davis III and Jacknow, 1975; Klein *et al.*, 1974; Stonerook *et al.*, 1984; Yost and Wukasch, 1983). However, increasingly stringent trade effluent legislation have led to cleaner manufacturing technology and improved effluent treatment (Karvelas *et al.*, 2003), as well as a general reduction in manufacturing in western countries. The reduced industrial emissions have proportionally increased the contribution from more dilute diffuse sources such as traffic related emissions (*e.g.* vehicle exhaust, brake linings, tyres, asphalt wear, gasoline/oil leakage), effluents from small businesses (*e.g.* car washes, dental uses), domestic effluents (*e.g.* metals leaching from household pipes, especially copper, and derived from household goods such as detergents), buildings (*e.g.* copper roofing material, galvanized steel as a zinc source, drainage water) and several other chemical treatment processes (Karvelas *et al.*, 2003; Sörme and Lagerkvist, 2002). Metal concentrations in wastewater thus vary widely between locations (Table 2.2).

Table 2.2 Mean toxic metal concentrations (μg l^{-1}) in wastewater from different localities (Ziolko *et al.*, 2009)

Location	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference
Whitlingham, UK, 1987	2.2	25.4	289	50	1.6	26	346	Lester, 1987a
Oxford, UK, 1979	6	63	161	158	-	40	1650	Lester *et al.*, 1979; Stoveland *et al.*, 1979
Thessaloniki, Greece, 2003	3.3	40	79	39	-	770	470	Karvelas *et al.*, 2003
Mean, highly polluted waters	*3.8*	*42.8*	*176.3*	*82.3*	*1.6*	*278.7*	*822*	
% SD, highly polluted waters	*2*	*19*	*105.8*	*65.8*	*-*	*425.6*	*719.7*	
Takatori, Japan, 1991	0.9	5.1	64	18	-	6.7	224	Chino *et al.*, 1991
Hendriksdal, Stockholm, 2002	0.23	4	78	3.6	0.1	6.2	150	Sörme and Lagerkvist, 2002
Survey of 30 different WwTW, UK, 2006	0.8	12	78	25	0.5	14	155	Rule *et al.*, 2006
Ribeirão Preto, Brazil, 2007	0.2	6.9	17	37	0.1	-	79	Oliveira *et al.*, 2007
Mean, moderately polluted waters	*0.6*	*8*	*53.0*	*26.7*	*0.3*	*10.4*	*152.7*	
% SD, moderately polluted waters	*0.4*	*3.6*	*32.0*	*9.6*	*0.3*	*5.2*	*72.5*	
Overall mean	*1.9*	*22.3*	*109.4*	*47.2*	*0.6*	*143.8*	*439.1*	
Overall % Standard Deviation (SD)	*108*	*99*	*82*	*108*	*123*	*213*	*125*	

Metals fate in conventional activated sludge processes (ASPs, Figure 2.1a) has been extensively studied over the past 30 years. Publications within the past 3-4 years alone include studies of nitrification inhibition (You *et al.*, 2009; Dionisi *et al.*, 2007) and biosorption (Pagnanelli *et al.*, 2009; Hammaini *et al.*, 2007; Al-Qodah, 2006; Yuncu *et al.*, 2006), as well as examination of their fate in pilot or full-scale plants (Conklin *et al.*, 2007; Carletti *et al.*, 2008). Metals in wastewater may occur as attached to suspended solids *via* surface bound organic ligands or adsorbed on to a major insoluble matrix component (*e.g.* iron(III) oxide, aluminium hydroxide, *etc.*); insoluble salts; inorganic complex solids, or as free or organically bound soluble forms; their speciation may depend on the influent metal concentration, influent chemical oxygen demand (COD), hardness, alkalinity and pH of the wastewater (Lester, 1987b). Their relative distribution can be estimated from the volatile suspended solid (VSS) fraction, roughly equating to the surface-bonded organic ligands, the non-volatile suspended solids (NVSS), which represents the insoluble matter, and soluble COD which includes the soluble organic ligands (Kempton *et al.*, 1987; Rossin *et al.*, 1982). Since metals are not biodegradable, their removal by a biological process is dependent on physicochemical processes, and ultimately partitioning between soluble and insoluble species according to the above fractions. Their removal during biological treatment can be by adsorption of soluble metal by the bioreactor activated sludge flocs and/or by settlement of the insoluble metal species with the sludge in the secondary settlement tank (Sterritt and Lester, 1981), and several factors thereby impact on their removal:

- plant operation parameters such as sludge age, hydraulic residence time (HRT), dissolved oxygen concentration and suspended solids removal which determine bulk sludge quality such as mixed liquor suspended solids concentration (MLSS) and stirred sludge volume index (SSVI) (Rossin *et al.*, 1982; Chen *et al.*, 1974; Stoveland, 1978; Brown *et al.*, 1973; Barth *et al.*, 1965),

- physicochemical parameters such as metal type, species and concentration, metal salt solubility, temperature, pH, concentration of chelating agents and particle size (Oliver and Cosgrove, 1974; Stumm and Bilinski, 1973; Cheng *et al.*, 1975; Rudd *et al.*, 1984; Stoveland and Lester, 1980; Nelson *et al.*, 1981; Fristoe and Nelson, 1983; Sterritt and Lester, 1983; Tien and Huang, 1991; Tien and Huang, 1987; Fukushi *et al.*, 1996; Wang *et al.*, 1999; Ledin, 2000; Lebeau *et al.*, 2002; Esparza-Soto and Westerhoff, 2003; Wang *et al.*, 2003; Ozdemir *et al.*, 2003; Pardo *et al.*, 2003; Savvaidis *et al.*, 2003; Comte *et al.*, 2008) and

- biochemical species, and specifically the extracellular polymeric substances (EPS) concentration (Rudd *et al.*, 1984; Tien and Huang, 1987; Fukushi *et al.*, 1996; Ozdemir *et al.*, 2003; Pardo *et al.*, 2003; Savvaidis *et al.*, 2003; Comte *et al.*, 2008; Brown and Lester, 1982b; Brown and Lester, 1982a; Brown and Lester, 1979; Guibaud *et al.*, 2003; Liu *et al.*, 2001; Comte *et al.*, 2006).

It follows that maximizing metals removal demands minimisation of soluble species and the improvement of solids removable by clarification.

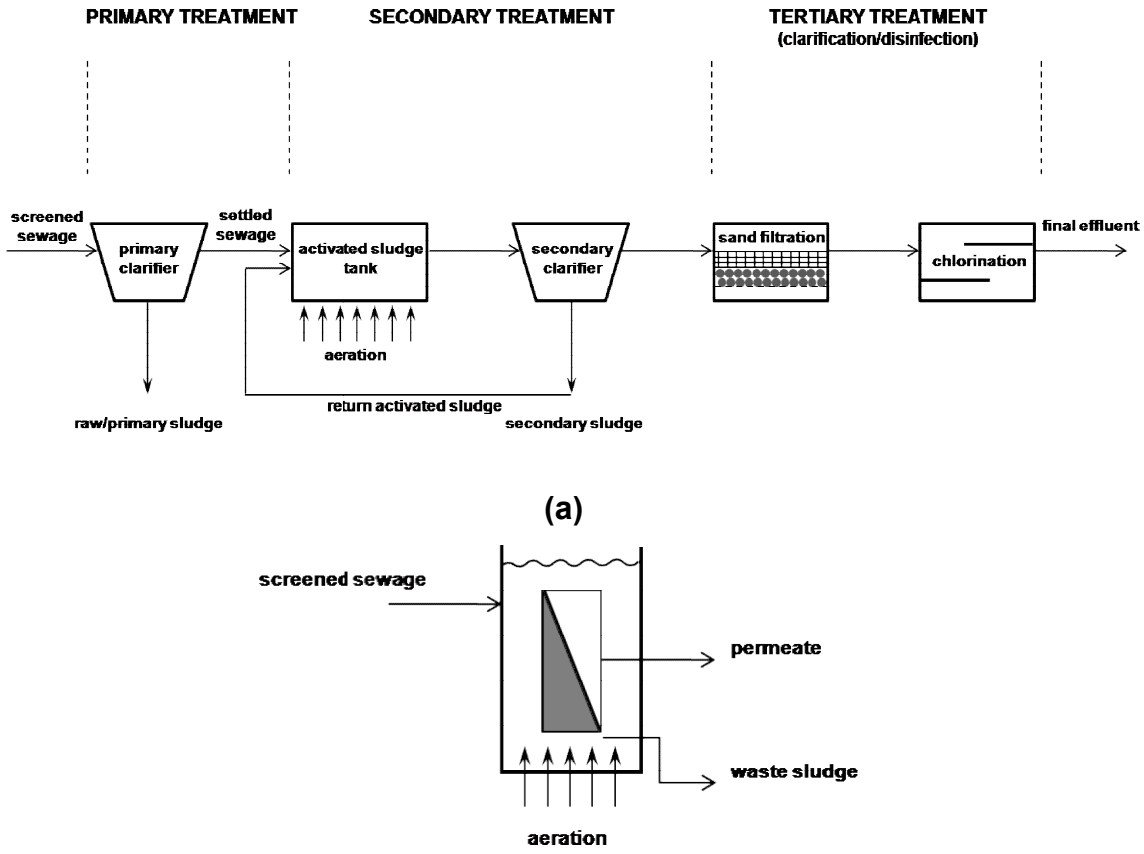

Figure 2.1 The activated sludge process (ASP) (a) and the membrane bioreactor (MBR) (b)

2.3 Membrane bioreactors and metals in wastewater treatment

The advantages offered by membrane bioreactors (MBRs, Figure 2.1b) for the treatment of wastewaters are well documented. These relate primarily to the high quality effluent produced, with effluents ostensibly free of suspended solids and pathogens, and the process intensivity, provided by its small footprint compared to the classical ASP (Judd, 2008). However, their hydraulic performance is limited by fouling of the membrane surface, an extensively studied phenomenon and recently comprehensively reviewed (Meng *et al.*, 2009), and clogging or blocking of the channels between the membranes (Judd, 2008), which is almost entirely unexplored.

The study of metals in wastewater, as they relate to MBRs, largely falls into three groups:

- use of metal-based coagulants for anti-fouling (Zhang *et al.*, 2008),
- treatment of metals-laden industrial effluents (Zaloum *et al.*, 1994; Chuichulcherm *et al.*, 2001; Canter, 2006), and
- fate of metal micropollutants in municipal and industrial wastewater treatment (Fatone *et al.*, 2006; Cattaneo *et al.*, 2008).

An advantage of an MBR is its ability to operate with uncoupled hydraulic and solids retention times (HRT and SRT respectively). Operation at long SRTs allows a smaller footprint plant with lower sludge production, and also high MLSS concentrations which tend to provide better nitrification (Judd, 2008). The impact of MLSS on metals removal is thus a key consideration for MBRs, as well as the more significant aspect of the retention of all suspended solids.

2.4 Metals removal by conventional ASPs

Metals removal by classical biotreatment is, for the reasons outlined in 2.2, vagarious, and values have been found to vary widely (Table 2.3). Of key importance is the source of the wastewater, municipal, industrial or a combination of both, which impacts primarily on metal type, speciation (and specifically solids:liquid partitioning) and concentration. The performance of a conventional ASP thus depends to some extent on that of the upstream primary settler and the downstream secondary clarifier, since the former reduces the solids loading and the latter reintroduces solids in the return activated sludge. Whilst primary settlement removes metals associated with settleable particles, a significant colloidal or dissolved fraction passes through to the biological secondary treatment (Lester, 1987b).

Iron (Fe) and aluminium (Al) are used as coagulants, though mainly in potable water treatment and can reach concentrations of several mg l^{-1} both in municipal and industrial wastewaters (Carletti *et al.*, 2008). Aluminium, a basic metal, has been measured at concentrations between 400 and 2500 $\mu g\ l^{-1}$ and removed at efficiencies of between 44 and 95% (Carletti *et al.*, 2008; Fatone *et al.*, 2006). A similar trend is evident with Fe, which also forms a sparingly soluble trivalent hydroxide, where concentrations have ranged from 480 to 2400 $\mu g\ l^{-1}$ and removal efficiencies from 79 to 90% (Carletti *et al.*, 2008; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Buzier *et al.*, 2006), with only one exception where removal was low at 21% (Karvelas *et al.*, 2003) which also coincide with the lowest influent concentration.

Table 2.3 Toxic metal concentration (μg l^{-1}) in wastewater and their removal (%) by conventional ASP

	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Reference
Concentration	3.3	40.0	79.0	39.0	-	770.0	470.0	Karvelas *et al.*, 2003
% removal	55	50	58	31	-	44	43	
Concentration	20.0	-	90.0	50.0	-	-	460.0	Chipasa, 2003 [a]
% removal	14	-	52	34	-	-	88	
Concentration	0.6	9.0	65.0	18.0	-	11.0	-	Buzier *et al.*, 2006
% removal	50	67	73	78	-	27	-	
Concentration	9.6	37.5	35.3	6.8	2.4	26.0	810.0	Carletti *et al.*, 2008
% removal	98	61	83	70	68	80	63	
Concentration	6.0	-	161.0	158.0	-	-	-	Lester *et al.*, 1979
% removal	88	-	96	93	-	-	-	
Concentration	-	63.0	-	-	-	40.0	1650.0	Stoveland *et al.*, 1979
% removal	-	68	-	-	-	75	95	
Concentration	21.0	177.5	193.5	524.5	-	104	809	Davis III and Jacknow, 1975 [a]
% removal	67	74	65	79	-	12.5	69	
Concentration	6.0	290.0	310.0	230.0	7.0	330.0	2400.0	Oliver and Cosgrove, 1974
% removal	83	79	74	94	86	18	77	
Concentration	6.0	80.0	90.0	270.0	-	70.0	600.0	Fristoe and Nelson, 1983
% removal	50	63	33	81	-	29	58	
Concentration	18.0	59.0	170.0	160.0	-	-	353.0	Brown *et al.*, 1973
% removal	11	78	61	43	-	-	48	
Concentration	1.8	38.0	56.0	62.0	2.8	28.0	-	Fatone *et al.*, 2008
% removal	90	60	55	69	>95	25	-	
Concentration	0.3	18.8	43.4	9.6	8.0	9.7	427.3	Fatone *et al.*, 2006
% removal	12	66	79	62	98	79	66	

[a] Average of the initial concentration and percentage removal from different wastewater types: municipal and industrial wastewater; (-) not specified

Other transitional metals have been found in a wide range of concentrations (Table 2.2 and Table 2.3), but generally lower than Fe. Cadmium (Cd) is present at low levels, with some peak concentrations (0.3 to 21 μg l^{-1}). Relatively poor removals (12-14%) have been recorded by a number of authors (Chipasa, 2003; Brown *et al.*, 1973; Fatone *et al.*, 2006), whilst other authors observed much removal (50-98%) at similarly low influent levels of 0.6 to 9.6 μg l^{-1} (Lester *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Oliver and Cosgrove, 1974; Buzier *et al.*, 2006; Fatone *et al.*, 2008; Roberts *et al.*, 1977). Cobalt (Co) has been also measured at low levels (2 μg l^{-1}) and removed at efficiencies of 36-50% (Fatone *et al.*, 2006; Buzier *et al.*, 2006). For manganese (Mn), the influent concentration tends to be higher 60-120 μg l^{-1} but not significantly better removed (33-72%) (Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Oliver and Cosgrove, 1974). Copper (Cu), nickel (Ni) and chromium (Cr) were measured at variable influent levels of 35-310 μg l^{-1} (Chipasa, 2003; Lester *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Buzier *et al.*, 2006; Fatone *et al.*, 2008; Roberts *et al.*, 1977), 9.7-770 μg l^{-1} (Stoveland *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Buzier *et al.*, 2006; Fatone *et al.*, 2008; Roberts *et al.*, 1977) and 9-290 μg l^{-1} (Stoveland *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Buzier *et al.*, 2006; Fatone *et al.*, 2008; Roberts *et al.*, 1977), respectively, with the corresponding removal efficiency ranges being 33-96%, 18-80% and 50-79%. Mercury (Hg) has been found at much lower levels (2.4-8 μg l^{-1}) but is removed by up to 68-98% (Carletti *et al.*, 2008; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Fatone *et al.*, 2008) with an exception of 17% removal at influent concentration of 1 μg l^{-1} (Brown *et al.*, 1973). Lead (Pb) also has variable influent concentration but is also generally removed at efficiencies ranging from 31 to 94% (Chipasa, 2003; Lester *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Buzier *et*

al., 2006; Fatone *et al.*, 2008; Roberts *et al.*, 1977). Finally, zinc (Zn), the most abundant transitional metal in wastewater, is generally removed at efficiencies between 43 and 95% (Chipasa, 2003; Stoveland *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Carletti *et al.*, 2008; Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Fatone *et al.*, 2006; Roberts *et al.*, 1977). The metalloid arsenic (As) is often present at low levels, average influent concentrations of 4.3 $\mu g\ l^{-1}$, and removed at efficiencies between 9 and 60% (Carletti *et al.*, 2008; Fatone *et al.*, 2006; Fatone *et al.*, 2008).

2.5 Metals removal by MBRs

Since MBR membranes are able to reject, by size exclusion, all particulate matter above 0.1 µm in size (Judd, 2008; Meng *et al.*, 2009) removal of metals associated with suspended solids would be expected to be quantitative. According to the metals removal data listed in Table 2.4, removals of over 95% total metal have been recorded for five of the seven metals (the exceptions being Ni and Zn). This would appear to indicate that metals arise primarily in the suspended form or else substantially precipitate in the treatment process. Even metals present at low concentrations tend to be significantly removed by MBRs: for example Co, measured at a influent concentration of 2.6 $\mu g\ l^{-1}$, has been shown to be 77-85% removed (Cecchi *et al.*, 2003).

Impacts of SRT (or, by implication, MLSS concentration) appear to vary. For example, for the ubiquitous Al and Fe – widely used coagulants in potable water treatment – removals range from 89 to above 99% and 77 to 98% respectively. The removal efficiency increases with increasing SRT by 8-11% and around 10% for Al and Fe respectively over a SRT range of 190 up to >300 days in both cases (Conklin *et al.*, 2007; Carletti *et al.*, 2008; Fatone *et al.*, 2006; Cecchi *et al.*, 2003; Innocenti *et al.*, 2002; Fatone *et al.*, 2005). Other metals where improved retention at longer SRTs has been demonstrated include Co, Cr, Cu, Ni, Pb and Zn. Increasing MLSS concentration from 3 to 10 $g\ l^{-1}$ has been shown to increase Cr(III) removal from 45 to 90%, since Cr(III) ions have

high affinity for the biomass flocs and are subsequently effectively retained by the membranes (Figure 2.2; Malamis *et al.*, 2009); an increase in SRT from 10 to 30 days was shown to increase Cr removal from 56 to 85% (Conklin *et al.*, 2007), the removal efficiency of Ni and Pb increases from 40 to 89% and 50 to >98% respectively on increasing the SRT from 11 to >1000 days (Fatone *et al.*, 2008; Cecchi *et al.*, 2003; Fatone *et al.*, 2005). The removal efficiency for Zn, one of the most abundant of the transitional metals and measured at concentrations up to 1.2 mg l^{-1} (Carletti *et al.*, 2008), has been shown to increase from 51 to 94% on increasing the SRT from 10 to >300 days (Conklin *et al.*, 2007; Cecchi *et al.*, 2003; Innocenti *et al.*, 2002). Overall, evidence suggests increasing SRT and/or MLSS tends to increase removal efficiency of most metals by between 12 and 66%, but it also appears that a threshold concentration is reached at very high SRTs (>1000 days) (Fatone *et al.*, 2008).

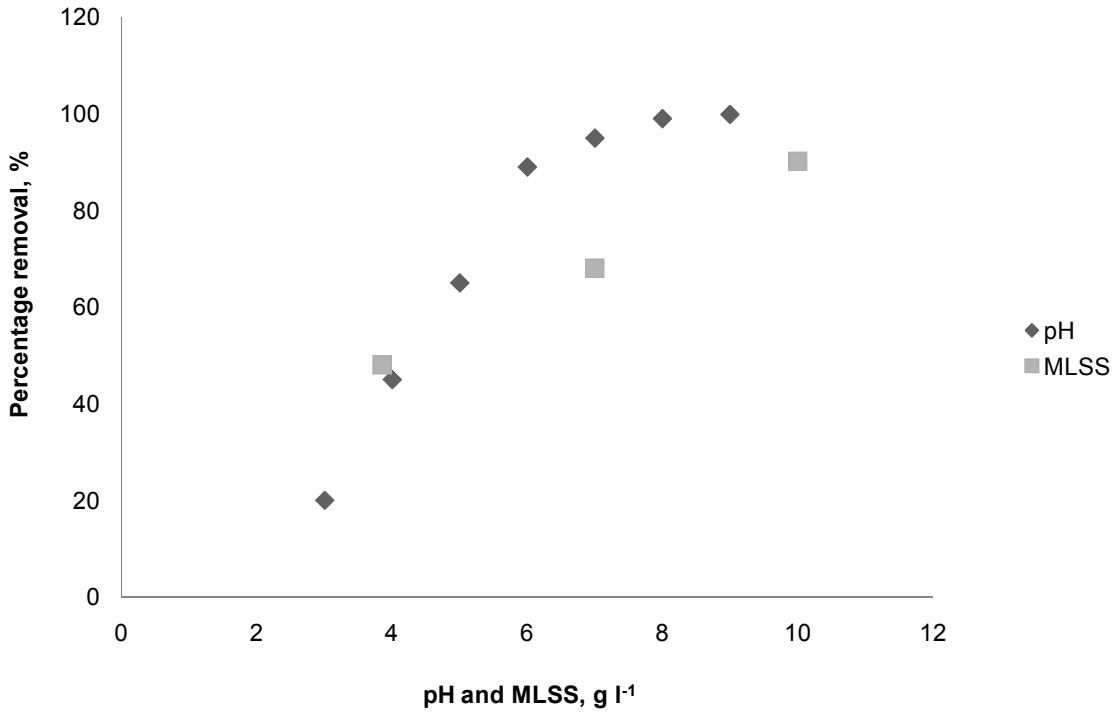

Figure 2.2 Chromium removal *vs* MLSS and pH (Malamis *et al.*, 2009)

Table 2.4 Toxic metal influent concentration (μg l^{-1}) in wastewater and their removal (%) by MBRs

	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Conditions	Reference
Concentration	0.3	18.8	43.4	9.6	7.95	9.71	427.3	4.8-9 g l^{-1} MLSS	Fatone *et al.*, 2006
% removal	>27	75	95	74	94	86	94	40-60 d SRT	
Concentration	1.8	38.0	56.0	61.7	2.8	27.8	-	11 d SRT	Fatone *et al.*, 2008
% removal	>90	>95	85	58	>95	40	-	4 g l^{-1} MLSS	
Concentration	1.8	38	56	61.7	2.8	27.8	-	200 d SRT	
% removal	>90	>95	89	63	>95	46	-	9 g l^{-1} MLSS	
Concentration	1.8	38.0	56.0	61.7	2.8	27.8	-	>1000 d SRT	
% removal	>90	>95	72	50	>95	66	-	18 g l^{-1} MLSS	
Concentration	1.8	38.0	56.0	61.7	2.8	27.8	-	>1000 d SRT	
% removal	>90	>95	90	70	>95	64	-	16 g l^{-1} MLSS	
Concentration	1.0	-	53.0	50.0	1.2	74.0	274.0	190 d SRT	Cecchi *et al.*, 2003
% removal	>50	-	90	88	58	50	51	14 hrs HRT	
Concentration	1.0	-	53.0	50.0	1.2	74.0	274.0	>300 d SRT	
% removal	>50	-	79	>98	>92	89	94	14 hrs HRT	
Concentration	0.5	18.5	53.9	9.6	8.0	8.7	461.0	55-67 d SRT	Fatone *et al.*, 2005
% removal	>50	75	96	74	94	79	>90	8 hrs HRT	
Concentration	-	-	-	-	-	-	-	190 d SRT	Innocenti *et al.*, 2002
% removal	>99	-	89	65	-	45	54	14 hrs HRT	
Concentration	-	-	-	-	-	-	-	>200 d SRT	
% removal	>99	-	72	50	>99	65	80	14 hrs HRT	
Concentration	-	-	-	-	-	-	-	10 d SRT	Conklin *et al.*, 2007
% removal	-	56	75	>68	97	32	59		
Concentration	-	-	-	-	-	-	-	20 d SRT	
% removal	-	-	81	-	95	-	-		

	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Conditions	Reference
Concentration	-	-	-	-	-	-	-	30 d SRT	
% removal	-	85	89	-	98	-	66		
Concentration	-	56.6	9.8	8.6	0.7	16.6	1233.0	-	Carletti *et al.*, 2008
% removal	-	72	90	74	92	72	83		
Concentration	-	-	-	-	-	-	-	18.4 d SRT	Cattaneo *et al.*, 2008
% removal	80	-	-	90	95	-	-	7.9 hrs HRT	
Concentration	-	746.0	1345.0	16.0	-	33.7	-	-	Dialynas and Diamadopoulos, 2009
% removal	-	89	49	100	-	100	-	-	

(-) not specified

Metals showing no impact of SRT tend to be present at low concentrations or else are substantially retained by the biomass. Cadmium, which is thought to have a high affinity for biomass or biomass-bound ligands (Brown and Lester, 1982a; Battistoni *et al.*, 2007), is almost completely removed either by membrane separation processes or conventional activated sludge processes with subsequently little increase with SRT (Fatone *et al.*, 2008; Cecchi *et al.*, 2003). Silver (Ag), removed by 90-99% (Conklin *et al.*, 2007; Cecchi *et al.*, 2003; Innocenti *et al.*, 2002), is similarly unaffected by SRT, as are other non-abundant metals such as vanadium (V) (Cecchi *et al.*, 2003; Innocenti *et al.*, 2002). Likewise, little or no increase in retention with SRT has been demonstrated for As, whose average influent concentration is below 4 $\mu g\ l^{-1}$ (Conklin *et al.*, 2007; Fatone *et al.*, 2006; Cattaneo *et al.*, 2008; Fatone *et al.*, 2008; Cecchi *et al.*, 2003; Fatone *et al.*, 2005) and for which considerable variation in removal (3-69%) has been reported. Increasing the SRT from a range of 11 to >1000 days, increased removal only marginally, from 3 to 37%, according to two studies (Fatone *et al.*, 2008; Cecchi *et al.*, 2003).

Conflicting data has been published for some species. Retention of Hg, which has been recorded at concentrations of 1.2-8 $\mu g\ l^{-1}$ (Carletti *et al.*, 2008; Fatone *et al.*, 2006; Cecchi *et al.*, 2003; Fatone *et al.*, 2005; Fatone *et al.*, 2008), has been shown to be unaffected by SRT in some cases (Conklin *et al.*, 2007; El-Din *et al.*, 2004) but to increase with SRT in others (Fatone *et al.*, 2008; Cecchi *et al.*, 2003; Innocenti *et al.*, 2002). For Cu, which is relatively abundant and ubiquitous in wastewaters, removal has generally been shown to increase with SRT (Conklin *et al.*, 2007; Fatone *et al.*, 2008; El-Din *et al.*, 2004). However, decreased removal with increasing SRT reported by some authors (Cecchi *et al.*, 2003; Innocenti *et al.*, 2002) has been attributed by them to a concomitant increase in organic matter. Lead has also been shown to decrease removal with increasing SRT (Fatone *et al.*, 2008; Innocenti *et al.*, 2002), other than for a single anomaly which was attributed to inconsistent influent concentrations (Jiang, 2001).

The impact of pH adjustment and coagulant dosing has been studied by some authors. Copper removal has been shown to be substantially increased by alum addition along with an extended SRT, with removals increased from 64 to 80% through dosing with alum and further increased to 94% on increasing the SRT from 30 to 50 days. pH adjustment had comparatively little impact on removal efficiency over a narrow range (7.4 to 8.3) (El-Din *et al.*, 2004). On the other hand, Cr, which occurs in environment in oxidation states of III and VI with some pH dependency, has shown to be more effectively removed on increasing the pH from 3 to 9 due to formation of the Cr(III) hydroxide precipitate above pH~6 (Malamis *et al.*, 2009). Adsorption onto the biomass flocs is also increased, and solids retention by the membranes subsequently yields higher removals (Malamis *et al.*, 2009). However, the pH of wastewater treatment works biomass in practice rarely rises above a value of 8.

2.6 MBR *vs* ASP data

There have been a large number of bench-scale studies devoted to elucidating the mechanism for metals removal by ASP or MBR biomass, many of which have been based on the premise that metals complexation by natural organic ligands in the wastewater significantly impact on their removal (Pagnanelli *et al.*, 2009; Hammaini *et al.*, 2007; Al-Qodah, 2006; Yuncu *et al.*, 2006; Oliver and Cosgrove, 1974; Stumm and Bilinski, 1973; Cheng *et al.*, 1975; Rudd *et al.*, 1984; Nelson *et al.*, 1981; Fristoe and Nelson, 1983; Sterritt and Lester, 1983; Tien and Huang, 1991; Tien and Huang, 1987; Fukushi *et al.*, 1996; Wang *et al.*, 1999; Ledin, 2000; Lebeau *et al.*, 2002; Esparza-Soto and Westerhoff, 2003; Wang *et al.*, 2003; Ozdemir *et al.*, 2003; Pardo *et al.*, 2003; Savvaidis *et al.*, 2003; Comte *et al.*, 2008; Brown and Lester, 1982b; Brown and Lester, 1982a; Brown and Lester, 1979; Guibaud *et al.*, 2003; Liu *et al.*, 2001).

These studies have ranged from the identification and study of the protagonist organic functional groups (Pagnanelli *et al.*, 2009; Yuncu *et al.*, 2006; Tien and Huang, 1987; Fukushi *et al.*, 1996; Ledin, 2000; Esparza-Soto and Westerhoff, 2003; Brown and Lester, 1982b; Brown and Lester, 1982a; Guibaud *et al.*, 2003; Liu *et al.*, 2001) and the impact on the physicochemical interactions of factors such as temperature (Al-Qodah, 2006), the identity and concentration of ions in solution competing for the binding sites (Al-Qodah, 2006; Rudd *et al.*, 1984; Wang *et al.*, 2003; Ozdemir *et al.*, 2003; Savvaidis *et al.*, 2003; Comte *et al.*, 2008; Brown and Lester, 1982b; Brown and Lester, 1982a; Brown and Lester, 1979; Guibaud *et al.*, 2003; Liu *et al.*, 2001), pH, bulk dissolved organic matter (DOM) concentration (Hammaini *et al.*, 2007; Nelson *et al.*, 1981; Fristoe and Nelson, 1983; Sterritt and Lester, 1983; Tien and Huang, 1991; Tien and Huang, 1987; Fukushi *et al.*, 1996; Wang *et al.*, 1999; Ledin, 2000; Lebeau *et al.*, 2002; Esparza-Soto and Westerhoff, 2003; Wang *et al.*, 2003; Ozdemir *et al.*, 2003; Pardo *et al.*, 2003; Savvaidis *et al.*, 2003; Comte *et al.*, 2008), and process operational determinants such as HRT and SRT (Oliver and Cosgrove, 1974; Stoveland and Lester, 1980). MBRs may be expected to provide enhanced removal by adsorption than ASPs due to the higher MLSS

concentration at which they operate combined with the smaller floc size (Meng *et al.*, 2009).

Notwithstanding the extensive discussion and progress made in determining speciation and mechanisms generally, data trends from pilot and full-scale plant operation across different studies remain vagarious, as indicated in Table 2.3 and Table 2.4. No patterns in percentage removal with either metals type or chemical behavior can be discerned. The only consistent overall trend relates to outlet *vs* inlet concentration, which follows a simple power relationship for both the ASP (Figure 2.3) and the MBR (Figure 2.4) regardless of the metal, albeit with significant data scatter below the line of parity (effluent concentration = influent concentration). Thus for the aggregated data (Figure 2.5):

$$C_{out} = m\, C_{in}^{n} \qquad \textbf{(2.1)}$$

where m and n respectively take values of 0.37 and 0.95 for the ASP, and 0.16 and 0.99 for the MBR, the r^2 value being around 0.83 for both plots. On this basis the MBR reduces the residual metals concentration by, on average, more than a factor of two. This is somewhat at odds with the averaged data from the individual metals (Table 2.5) which suggest that the reduction in the effluent metals concentration afforded by the MBR compared with that of the ASP is between 19 and 50%, depending on the individual metal.

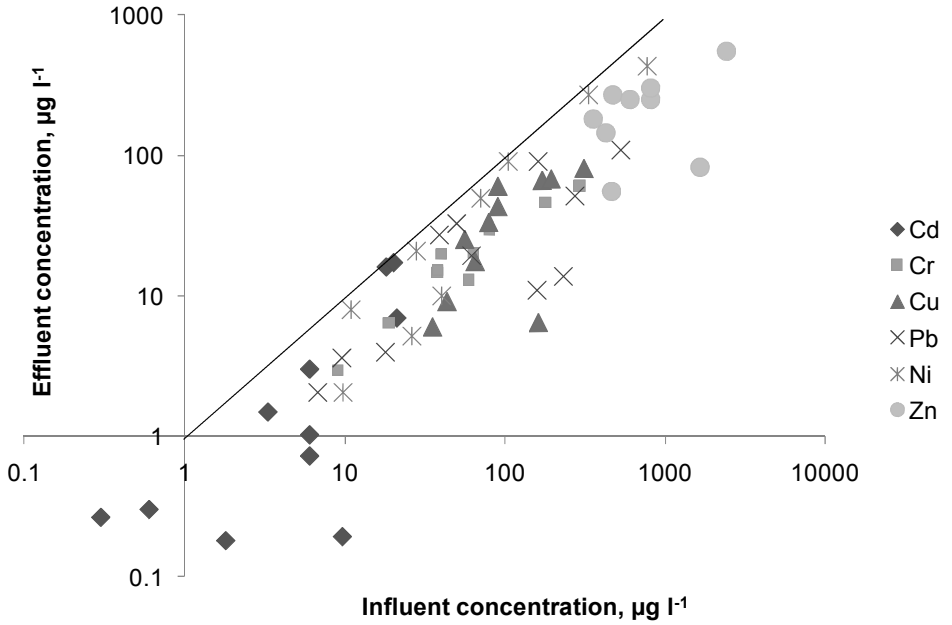

Figure 2.3 Effluent *vs* influent metals concentration, ASP data

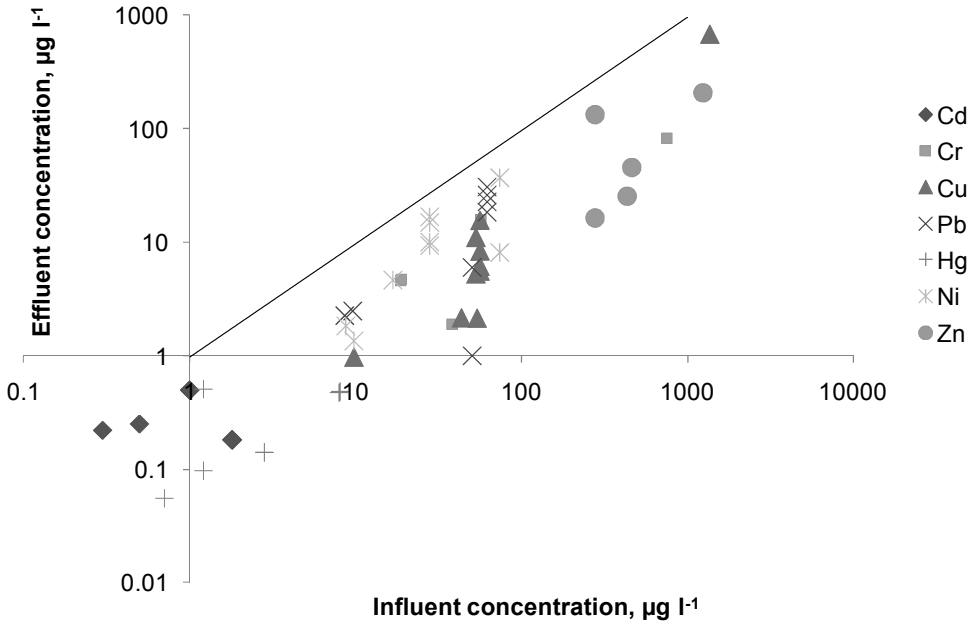

Figure 2.4 Effluent *vs* influent metals concentration, MBR data

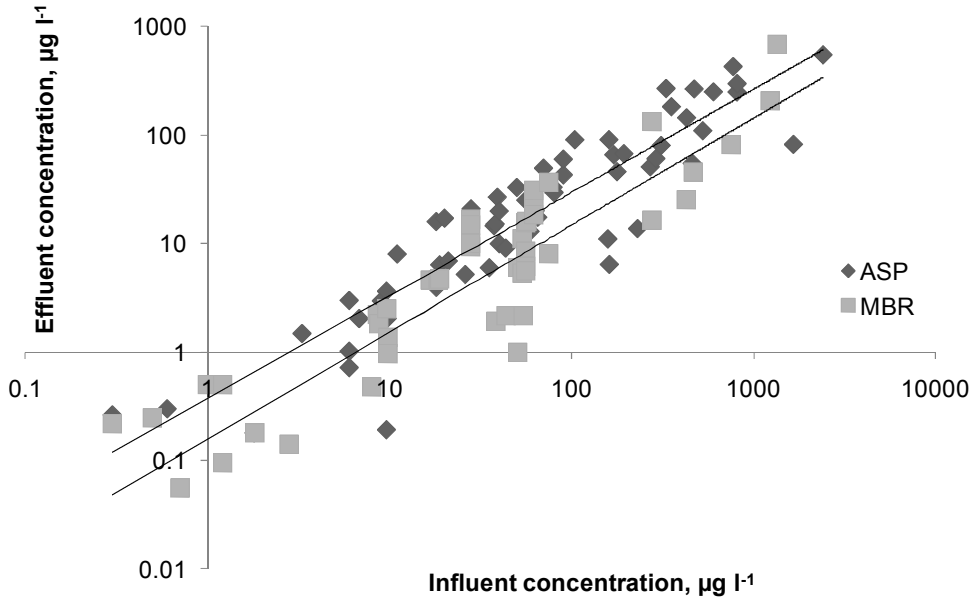

Figure 2.5 Effluent *vs* influent metals concentration, all data, ASP and MBR

Table 2.5 Mean and standard deviation (% SD) for ASP and MBR toxic metal influent concentration (µg l^{-1}) and removal efficiencies (%)

	Cd	Cr	Cu	Pb	Hg	Ni	Zn
ASP							
Mean Concentration	8.5	81.3	117.5	139.0	5.0	154.3	886.6
% SD	91	107	71	113	59	172	78
Mean % Removal	62	69	68	74	87	46	68
% SD	52	13	25	30	16	60	25
MBR							
Mean Concentration	1.3	124.0	178.2	39.1	3.4	32.8	533.9
% SD	50	203	230	63	81	71	75
Mean % Removal	74	83	83	73	92	64	75
% SD	34	16	15	22	11	32	23
Difference in % removal, MBR vs ASP	*18*	*17*	*16*	*6*	*6*	*21*	*7*
Mean % reduction in residual, MBR vs ASP	*41*	*50*	*49*	*19*	*43*	*37*	*22*

All evidence supports the premise that metals removal is predominantly by solids rejection, rather than adsorption of the dissolved species. In most cases at moderate concentrations (>1 μg l^{-1} in the influent), where data are available, the effluent dissolved concentration from ASP data is either the same or indeed higher than the influent concentration unless influenced by chemical changes directly impacting on salt solubility (such as pH, counter ion concentration or a change in oxidation state). This is reflected in published data for a number of the transitional metals, including Co, Cr, Cu, Fe, Ni, Pb and Zn (Karvelas *et al.*, 2003; Oliver and Cosgrove, 1974; Buzier *et al.*, 2006). Dissolved Mn on the other hand, which is subjected to change in oxidation state from soluble Mn(II) to insoluble Mn(IV) during aerobic treatment, has been shown to be significantly removed by an ASP (Karvelas *et al.*, 2003). Whilst the MBR might be expected to provide a higher capacity for the dissolved metals, due to the very significant increase in solid:liquid interfacial area of MBR sludge, this does not appear to be the case in practice.

2.7 Conclusions

Metals as micropollutants have been less extensively studied than the higher profile endocrine-disrupting organic substances (Sipma *et al.*, 2010), yet data for their removal extends back almost 40 years; they have recently attracted increased interest due to legislation such as WFD. A number of conclusions can be drawn from the body of work on metals removal by the conventional activated sludge process (ASP) and that from membrane bioreactors (MBRs):

- General trends suggest that MBRs offer slightly greater metals removal than ASPs, presumably through enhanced clarification provided by the membranes which are able to reject, by size exclusion, all particulate matter above 0.1 μm in size. The decrease in residual effluent concentration (Table 2.5) provided by the MBR compared with the ASP, based on the entire body of information provided in Table 2.3 and Table 2.4, is no more than 50%, Cu and Cr showing the most significantly improved removal. Aggregated graphical data (Figure 2.5) suggests an overall reduction of 57% on average.

- Removals by conventional ASPs followed the order Ni<Cd<Cu<Cr=Pb<Zn<Hg, *cf.* Ni<Pb<Cd<Zn<Cr<Cu<Hg for MBRs. Given the very broad scatter in the data, the small differences in the order of removal reported cannot be determined with any certainty. Moreover, and notwithstanding expectations based on equilibrium thermodynamics, there is no apparent trend in removal with increasing influent concentration either for ASPs or MBRs. On the other hand, some authors have claimed hydraulic retention time to have a significant impact on removal for conventional ASPs (Özbelge *et al.*, 2005), indicating that there may be a kinetic element in metal retention.

- Whilst some authors report an increase in removal with solids retention time, the increase is generally small and varies between

studies. For the ASP, the metal removal efficiency depends on factors such as MLSS, suspended solids removal and COD, factors which are linked to SRT such that the impact of the latter is not easily predicted and is dependent not only metal species but also on wastewater quality. Notionally, a higher SRT would be expected to provide increased capacity through a higher solids surface area for metals adsorption. This effect would then be expected to be enhanced in an MBR since flocs are generally smaller in size (Judd, 2008) and the membrane retains macromolecular materials in addition to particulates. It has been postulated that increased concentrations of dissolved organic at longer SRTs may actually promote dissolution of metals and lead to slightly elevated concentrations (Malamis *et al.*, 2009).

- Given the above findings, removal of metals down to very low levels is likely to demand tertiary polishing processes based either on chemical precipitation, adsorption or membrane nanofiltration to target the dissolved species, which evidence suggests will be substantially in complexed form. Whereas for other organic and ostensibly biodegradable micropollutants the installation of an MBR may be justified on the basis of their improved removal over that attained by a conventional ASP (Sipma *et al.*, 2010), the improvement in metals removal offered by an MBR is marginal in comparison. Given the high energy and voluminous waste generated by the MBR, it is questionable that the selection of this process technology for improved metals removal alone is justifiable either on a cost or carbon footprint basis.

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3 THE COMMERCIAL STATUS OF MEMBRANE BIOREACTORS FOR MUNICIPAL WASTEWATER

Ana Santos and Simon J. Judd

Published in Separation Science and Technology

Centre for Water Science, Cranfield University, Bedfordshire, UK

Abstract

The status of membrane products for membrane bioreactors is reviewed with specific reference to the municipal wastewater market. Products are identified according to their geographical location and characteristics. The latter are appraised with reference to the membrane configuration, polymeric material type, pore size and, for the hollow fibre (HF) products, the filament diameter. The market penetration of 11 of the suppliers is also assessed.

It is revealed that the time taken between the launch of a product and the installation of a large membrane plant (>10,000 m^3 d^{-1} capacity) based on that product has decreased significantly over the past 10 years, appearing to reflect on a growing acceptance of and confidence in the technology. Whilst the market continues to be dominated by the two most established suppliers, a number of new providers are emerging, in particular from Korea and China. The preferred polymeric membrane materials are polyvinylidene difluoride (PVDF) and polyethersulfone (PES), which account for around 75% of the total products on the market including 9 out of the 11 most commercially important products. There appears to be rather more diversity of material types and membrane element size in the HF products than in the flat sheet (FS) ones, notwithstanding the emergence of new non-rigid FS panels and the existence of FS rotating modules.

3.1 The market and the commercial technologies

The advantages offered by membrane bioreactors (MBRs) have been widely recognised for almost 50 years (Bemberis *et al.*, 1971), and by the early 1970s the first commercial technology was available (Dorr Oliver) with the Rhone Poulenc technology introduced subsequently. However, it is only since the introduction of the immersed configuration (iMBR) – some two decades after the original sidestream technology – that a rapid growth in its implementation and subsequent significant penetration of the substantial municipal has taken place (Judd, 2008). The MBR market value doubled in the five years between 2000 and 2005 to reach $217 and is expected to increase its market value from $296 million in 2008 to $488 million in 2013 (Hanft, 2008). Even with the slowing of growth brought about by the global financial crisis, the prospects for the technology appear auspicious.

It is therefore unsurprising that the number of available proprietary MBR membrane products has dramatically increased since the first iMBR technology was commercialised in 1990 (the Kubota ES flat sheet panel), followed by the second (the GE Zenon "Zeeweed®" hollow fibre module) in 1993 (Table 3.1). These two technologies retain their dominance of the global municipal MBR market today (Figure 3.1), with Kubota providing 39% of the total number of MBR installations for the top 11 MBR membrane providers (with respect to installed capacity) and GE Zenon around 46% of the total global installed capacity for MBR treatment; Mitsubishi Rayon Engineering (MRE) have almost as many installations as Kubota, but their activities are largely limited to the Far East. However, newer MBR membrane products are increasing in number and also in market share. As recently as 2003, the most established three players of Kubota, MRE and GE Zenon had 85-90% of the municipal MBR market, with around 800 installations between them (Pearce, 2008). By mid 2009 this number had risen to over 3500 of the total of approaching 5000 municipal installations, with more than 20 other membrane suppliers with MBR reference sites for municipal wastewater treatment. Of the suppliers listed in Table 3.1, only a handful of them pre-date the year 2000 with regards to their original

product launch. Table 3.1 lists membrane suppliers according to membrane configuration with a few suppliers (*e.g.* Mitsubishi Rayon and Huber) providing more than one membrane product of a single configuration, and a one or two more (*e.g.* Orelis Environment and Ecologix) providing more than one membrane configuration. The commercially available MBR membrane products, their characteristics and suppliers geographical location were identified through searches of the internet, technical ("grey") literature, business networking sites and general active networking."

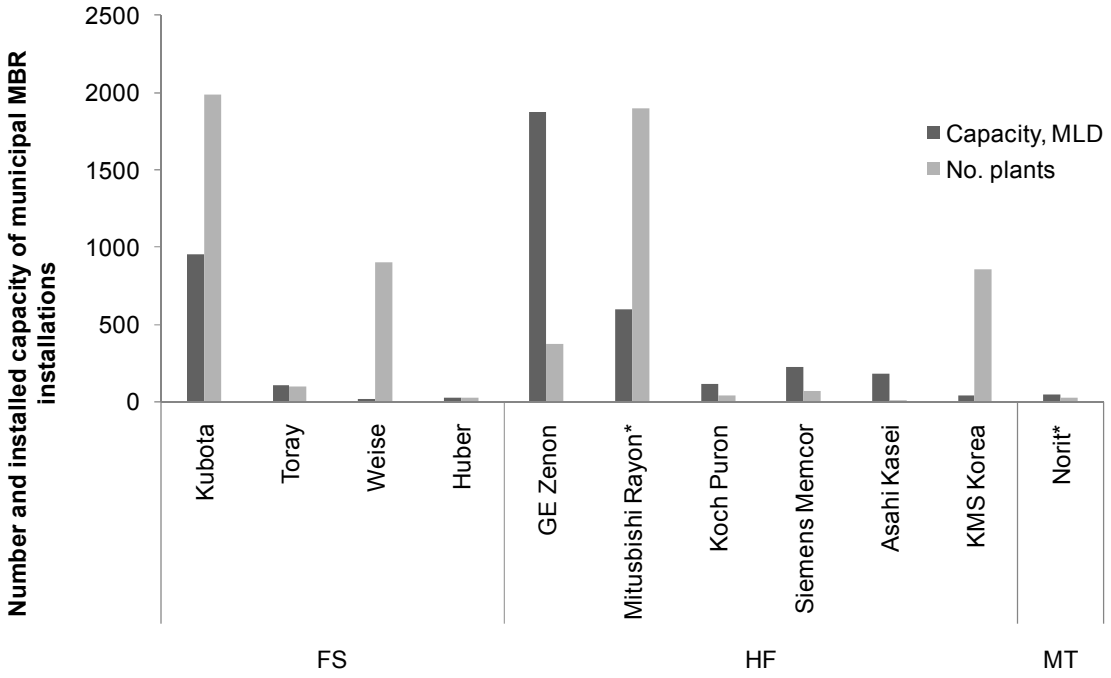

Figure 3.1 MBR municipal market; *estimated figures from available information

Table 3.1 Total MBR technologies reviewed

Immersed (iMBR)		Sidestream (sMBR)
Flat sheet	*Hollow fibre*	*Multitube/multichannel*
A3 – MaxFlow DE	Asahi Kasei – Microza™ JP	Berghof – HyPerm-AE; HyPerflux DE
Alfa Laval – Hollow Sheet SE	Beijing Origin Water Technology CN	Norit X-Flow – F4385, F5385 NL
Brightwater – MEMBRIGHT® IRL	Ecologix – EcoFlon™, EcoFil™ CN	Orelis Environment – Kerasep®; Pleiade® FR
Colloide – SubSnake NIR	ENE – SuperMAK KR	MEMOS – MEMCROSS DE
Ecologix – EcoPlate™, EcoSepro™ CN	GE Zenon – ZeeWeed® NA	
Huber – VRM®; ClearBox®, Biomem DE	Hangzhou H-Filtration Memb. Tech. & Eng. – MR CN	
Jiangsu Lantian Peier Membrane CN	Koch Membrane Systems – PURON® NA	*Hollow fibre*
KOReD – Neofil KR	Korea Membrane Separations – KSMBR KR	Ultra-flo – Ultra-flo® SG
Kubota – ES/EK JP	Litree Purifying Technology – LH3 CN	Polymem – IMMEM FR
MICRODYN-NADIR – BioCel® DE	Memstar Tech. – SMM SG	
Pure Envitech – ENVIS KR	Micronet Porous Fibers – Micronet® SP	*Flat disc ceramic*
Shanghai Megavision Memb. Eng. & Tech. CN	Mitsubishi Rayon Eng. – Sterapore SUR™; SADF™ JP	Kerafol DE
Shanghai SINAP Membrane Sci. & Tech. CN	Tianjin Motimo – Flat Plat FPII CN	Grundfos – Biobooster DK
Toray – MEMBRAY® TMR JP	Philos KR	
Vina Filter – VINAP CN	SENUO Filtration Technology – SENUOFIL CN	
Weise Water Systems GmbH – MicroClear® DE	Shanghai Dehong Biology Medicine Sci. & Tech. Dev. CN	
	Siemens Water Tech. – MemPulse™ DE	
	Sumitomo – POREFLON™ JP	
	Superstring MBR Technology – SuperUF CN	
	Vina Filter – F08 CN	
	Zena Membranes – P5 CZ	

CN: China/Taiwan; CZ: Czech Republic; DE: Germany; DK: Denmark; FR: France; IRL: Southern Ireland; JP: Japan; KR: Korea; NA: North America (USA/Canada); NIR: Northern Ireland; NL: Netherlands; SE: Sweden; SG: Singapore; SP: Spain

A review of the geographical location of the listed providers (Figure 3.2) reveals them to derive primarily from East Asia, with China, Korea, Japan and Singapore and providing over half of the technologies identified, and the EU, and principally Germany, providing most of the remainder. Moreover, there are a number of other MBR membrane products either currently close to being commercialised or already commercially available but not visible through the usual routes of internet search engines, international trade shows or articles/advertisement in trade magazines. Having said this, it is not always possible to distinguish between original membrane or membrane module manufacturers (*i.e.* original equipment suppliers, or OEMs) and those which simply acquire these products and rebrand them for sale.

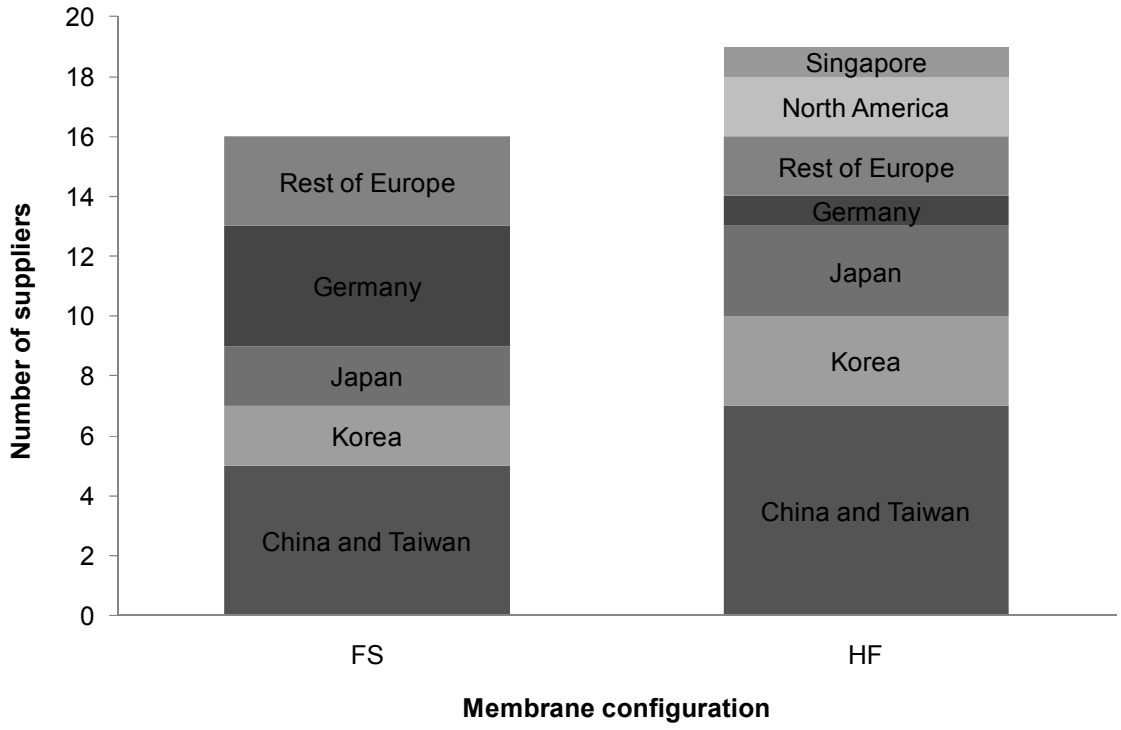

Figure 3.2 Global distribution of flat sheet (FS) and hollow fibre (HF) membrane suppliers

Some technologies have evolved over a number of years, with significant modification of the designs yielding different products. The original iMBR membrane module produced by GE Zenon, for example, was the Zeeweed® 145, containing 145 square feet of membrane area and in which the fibres were looped over a raised section of the frame. This design was subsequently superseded first by the ZW150 and then by the more familiar ZW500 module, for which there have been three generations with a fourth due shortly. The Kubota 510 membrane panel, on the other hand, has remained unchanged since its introduction in 1990 and was only supplemented by the larger 515 panel in 2008. MRE similarly introduced its SADF membrane module in 2004, a product significantly different in design to the original SUN module and which now forms the basis of all large municipal MBRs based on MRE technology.

Of the other technology suppliers, Huber (and also Martin Systems AG) both provide both classical rectangular panels and a more novel rotating FS configuration membrane. Some suppliers (*e.g.* Koch, MICRODYN-NADIR and Orelis Environment) provide membranes of different configurations, though in such cases it appears that only one configuration is actually marketed for MBR duty. A few vendors, particularly in China and Korea, provide a number of different dedicated MBR membrane configurations. For example, the company Ecologix in Taiwan provides HF membrane modules of two different membrane materials (PVDF and PTFE) and two distinct FS panels (a rigid and non-rigid variety, apparently available in PVDF, PES and PAN). Such extraordinary diversity from a single supplier, however, the products are too recent to have achieved substantial market penetration. Finally, there are some new ceramic products (Kerafol and the highly unusual Grundfos *Biobooster*) which may come into use for industrial effluent treatment in the future.

It should be noted that some MBR technology suppliers employ other membrane products. This is particularly evident with the sidestream technologies of process suppliers such as Aquabio in the UK, Parkson in the USA and Wehrle in Germany, all of whom employ multitube (MT) membrane products for their technology, and primarily Norit but also Berghof and others.

Such diversity of suppliers is made possible by the standardisation of MT membrane modules, which are of thus a set diameter and length regardless of the membrane material and pore size. Hitachi and Busse similarly employ proprietary flat sheet panel products in their technologies, both of them achieving success through specialising in package plants for specific applications. These examples reflect the wider issue of the importance of the design of the overall MBR technology, and not just than of the membrane module.

Recent reviews in the EU market (Lesjean and Huisjes, 2008; Lesjean *et al.*, 2009) have revealed rapid growth in this region, which reflects growth encountered elsewhere in the world. These reviews have shown the EU in particular to be dominated by the two leading suppliers, in that as at the end of 2008 all of the large MBRs (>10 megalitres *per* day, or MLD, in capacity) were either Kubota or Zenon. There were also noted regional differences, with all such large MBR installations in Italy (4 off), and the Netherlands, Switzerland, Belgium, Cyprus and Hungary (one each) being GE Zenon. A more equal distribution (of the 32 installations in total across the EU) between Kubota and GE Zenon was reported for Germany, Spain and the UK. However, other technologies have a presence in the EU, and the Netherlands in particular has well established national programme for demonstrating a range of MBR technologies at reasonable scales.

Globally, there is also a pronounced upward trend in plant size, reflecting noted trends reported for the EU by Lesjean *et al.* (2008; 2009), as unsurprisingly dominated by GE Zenon (Table 3.2) who provide 15 of the 20 largest plant (as of end 2009); in terms of the average flow capacity the company still accounts 13 of the top 20. However, a review of the largest installations, including those in planning or construction and due before 2011, for individual technologies (Table 3.3) reveals that some Far Eastern suppliers, with products launched only within the past few years, have been able to secure contracts for very large projects – particularly in China and the Middle East.

Table 3.2 Top 20 largest MBR installations globally

Project, Country or US State	*Supplier*	*Date*	*PDF, MLD*	*ADF, MLD*
Wenyuhe, China	Asahi Kasei	2007	100	100
Johns Creek, Georgia	GE Zenon	2009	94	41
Beixiaohe, China	Siemens Water	2008	78	60
Al Ansab, Muscat, Oman	Kubota	2009	78	56
Peoria, Arizona	GE Zenon	2008	76	38
Cleveland Bay, Australia	GE Zenon	2007	75	29
Lusail, Qatar	GE Zenon	2008	60	60
Cairns North, Australia	GE Zenon	2009	58	19
Cairns South, Australia	GE Zenon	2009	58	19
Sabadell, Spain	Kubota	2009	55	35
San Pedro del Pinatar, Spain	GE Zenon	2007	48	20
Syndial, Italy	GE Zenon	2005	47	38
Broad Run WRF, Virginia	GE Zenon	2008	47	38
Beijing Miyun, China	Mitsubishi Rayon	2006	45	30
Nordkanal, Germany	GE Zenon	2004	45	17
Tempe Kyrene, Arizona	GE Zenon	2006	44	34
Brescia, Italy	GE Zenon	2002	42	42
Traverse City, Michigan	GE Zenon	2004	39	27
Linwood, Georgia	GE Zenon	2007	38	17
North Kent Sewer Authority, Michigan	GE Zenon	2008	35	23

PDF: Peak daily (design) flow; ADF: Average daily (design) flow

The historical development of the technology is intriguing. For example, at the end of the last millennium, the largest MBR plant in the world was the plant at Swanage in the UK, with a design capacity of around 13 MLD. It was around that time that Norit first started developing their novel airlift sidestream configuration for municipal wastewater applications, at a pilot plant in Vienna, before launching it as a commercial product in 2002. There are now around 30 plants worldwide based on this technology, with the largest of these being the 17 MLD plant at Palm Jumeirah in the UAE (Table 3.3), compared with the 237 Kubota plants in 1999 when Swanage was being commissioned. This means

that, in less than a decade, a technology based on a novel configuration (*i.e.* airlift sidestream) has grown to the point where the largest installation based on that technology exceeds the capacity of that of the largest installation ten years ago.

Table 3.3 Largest installations, operational by 2010, for individual technology providers; plants >10 MLD capacity

Location	Supplier	Date	Capacity, MLD
Jumeirah Golf Estates, UAE	GE Zenon	2010	189
Wenyuhe, China	Asahi Kasei/BOW	2007	135
Guangzhou, China	Memstar	2010	100
Beixiaohe, China	Siemens Water	2008	78
Al Ansab, Muscat, Oman	Kubota	2009	78
Najran, Saudi Arabia	Toray	2010	60
Beijing Miyun, China	Mitsubishi Rayon*	2006	45
Tianjin Industry, China	Tianjin Motimo	2007	30
Griffith, Australia	KMS Puron	2010	30
Daegu Dalsung, Korea	Korea Membrane Separation	2008	25
Ji'an, China	MICRODYN-NADIR	2010	20
Palm Jumeirah, UAE	Norit	2009	17

*SADF technology, introduced in 2004; UAE: United Arab Emirates

This would seem to reflect a more general trend in increasing acceptability of comparatively new technologies. Of the 12 technologies listed in Table 3.3, only two pre-date 2000 and many have less than 50 reference sites (Figure 3.1). Notwithstanding this some very large installations, the smallest being the Palm Jumeirah plant, are planned based on these technologies despite some of them being no more than 1-7 years old. This provides further evidence of the change in perception of MBRs as a "new" or high-risk technology: it appears that fewer reference sites are now required for a technology to be considered

commercially acceptable at a large scale. Indeed, a correlation of the time taken for a technology to achieve the first 10 MLD capacity plant provides a stark illustration of this, with the gestation time sharply decreasing since the turn of the millennium (Figure 3.3).

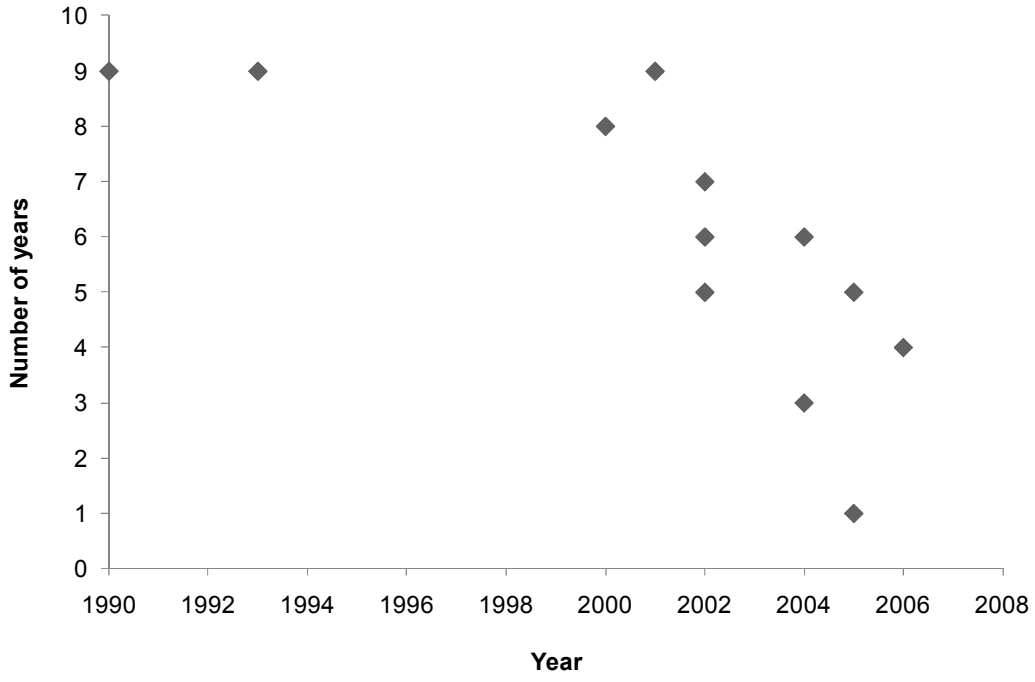

Figure 3.3 Time taken between product launch and installation of first plant of more than 10 MLD capacity for 12 MBR membrane products

3.2 The membranes

The membranes used in MBRs can be categorised according to their configuration (primarily their geometry and flow direction), material type, and physical size (Judd, 2008). All MBR membrane technologies are either flat sheet (FS), hollow fibre (HF) or multitube/tubular (MT/Tu), with the immersed process technologies exclusively comprising HF or FS membranes and the sidestream technologies being mainly MT, and they are almost exclusively polymeric: none of the ceramic membrane-based technologies are in general

use for MBRs. With regards to physical size, it is primarily the separation of membrane panels and the fibre (or filament) outside diameter which constitute the key dimension for the FS and HF configurations respectively, whereas it is the internal diameter for the MT products. Only the iMBR products are considered in the analysis below. Apart from the standardised MT products (Norit and Berghof), the other sMBR systems are varied, currently have little market penetration and are subject to different design criteria.

In the case of the FS configuration, all products for which information is available have a membrane separation between 6 and 10 mm. Almost all of the immersed systems apart from the two rotating membrane products (the Huber VRM and the Martin Systems *siClaro DM*) are rectangular panels around 0.5 m wide and 1-1.5 m deep. Purely in terms of the physical dimension of the panels, they are thus all quite similar. However, some of the newer products, specifically those from Alfa Laval, Colloide, MICRODYN-NADIR, and the new AGFA-Vito membrane (still under development but close to commercialisation) (Doyen *et al.*, 2010), are based on non-rigid, composite membrane panels which do not rely on a rigid plastic substrate of, for example, acrylonitrile butadiene styrene (ABS) plastic in the case of Kubota, for mechanical integrity. A slimmer membrane panel permits a higher packing density and potentially reduced production costs if the complete double-sided composite membrane can be produced continuously. Moreover, unlike the rigid FS panels but like HF membranes, these materials are backflushable. On the other hand, since these are new products their robustness over the long term use is currently unknown, whereas there are reference sites based on both Kubota and GE Zenon membranes which demonstrate membrane life of up to 11 years.

Polymer materials used for MBR membranes are largely limited to two fluorinated polymers (polyvinylidene difluoride, PVDF, and polytetrafluoroethylene, PTFE), two sulphonated polymers (polyethersulfone, PES, and polysulphone, PS) and two polyolefinic membranes (polypropylene, PP, and polyethylene, PE), with a pore size ranging from 0.01 to 0.4 µm (Figure 3.4). PES/PS membranes are mostly in the ultrafiltration pore size range and

make up 20% of the iMBR membrane materials listed. The PTFE and polyolefinic membranes, on the other hand, are all in the microfiltration range (0.08-0.4 µm). However, polyvinylidene difluoride (PVDF) membranes dominate, making up 55% of the total iMBR membrane technologies considered and cover almost the entire pore size range (between 0.04 and 0.4 µm). The only other polymeric membrane materials employed are polyacrylonitrile (PAN), employed in one sidestream HF product, and polyvinyl alcohol (PVA) in an immersed FS technology. There is a greater diversity of materials used for HF membranes than for FS ones, with those used for FS panels currently being largely limited to PES and PVDF, though the market leader (Kubota) employs a chemically modified PE material.

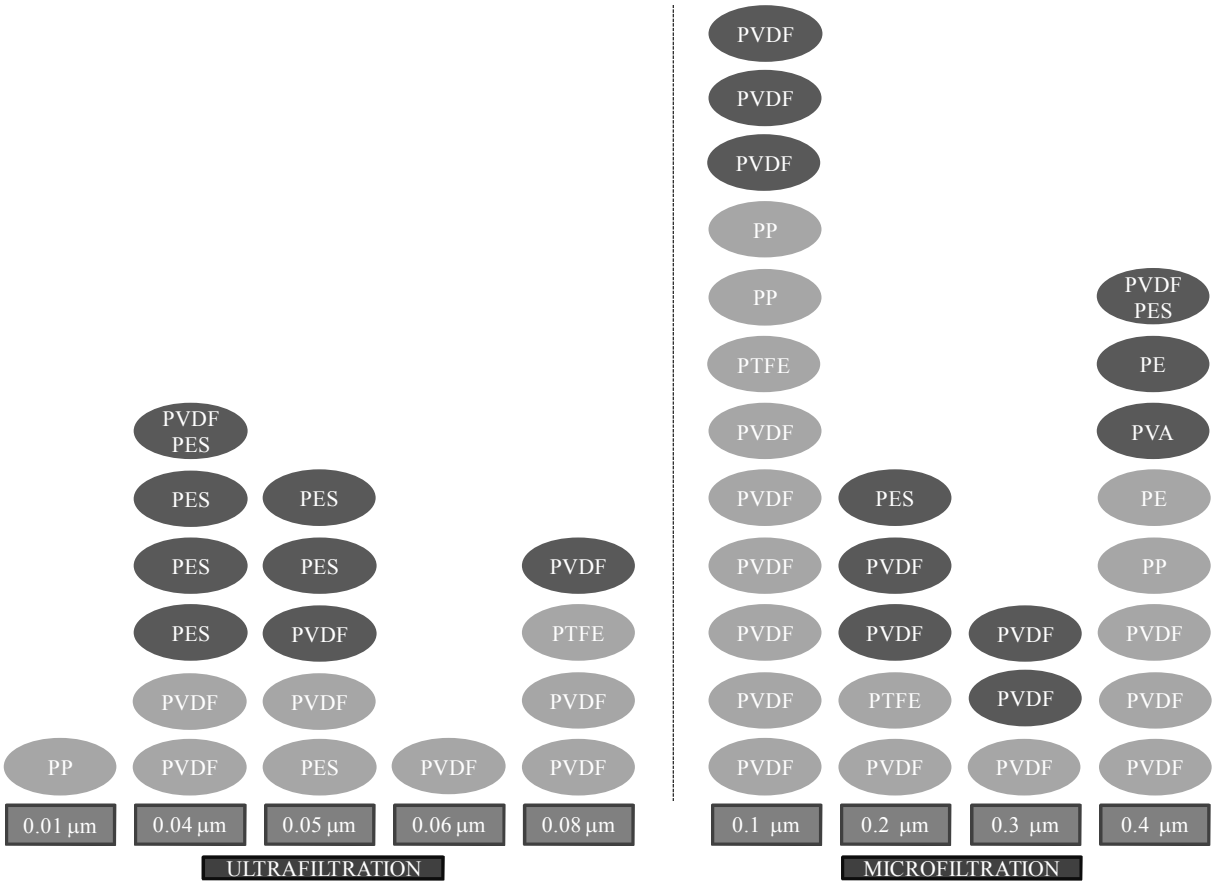

Figure 3.4 Membrane pore size *vs* membrane material (light shadow: HF; dark shadow: FS), immersed systems

A review of the facets of the different polymeric materials used for MBR membranes is beyond the scope of this paper, and both a comprehensive review (Meng *et al.*, 2009) and an excellent *précis* (Pearce, 2007) are available elsewhere. However, the most salient properties of the membrane material properties relate to their surface and bulk properties. The surface properties comprise the pore size distribution and the hydrophilicity, and the important bulk properties are chemical, thermal and mechanical integrity. All the membrane materials are naturally hydrophobic and have to be made hydrophilic either by blending with hydrophilic copolymers (as applies to PES/PS products), oxidative chemical post-treatment (possible for PE) or wetting out, normally using a reagent such as polyvinyl alcohol (PVA). The membrane materials are also thermo-tolerant beyond the 40ºC limit imposed by many of the membrane suppliers, but this threshold is determined by other constituents of the membrane module (specifically the potting compound).

Polyolefinic HF membranes are generally produced by the relatively simple process of dry spinning, which produces slit-like pores therefore having a wider pore size distribution. This, along with the relatively low pore density, tends to make the membrane more susceptible to fouling and thus necessitates lower-flux operation than that of other membrane materials. This can be countered to some extent by producing modules of higher packing density and thus smaller diameter filaments (Figure 3.5), and this is reflected in the commercial trends. However, the limitations of this material have meant that it has been largely superseded by the other polymeric materials.

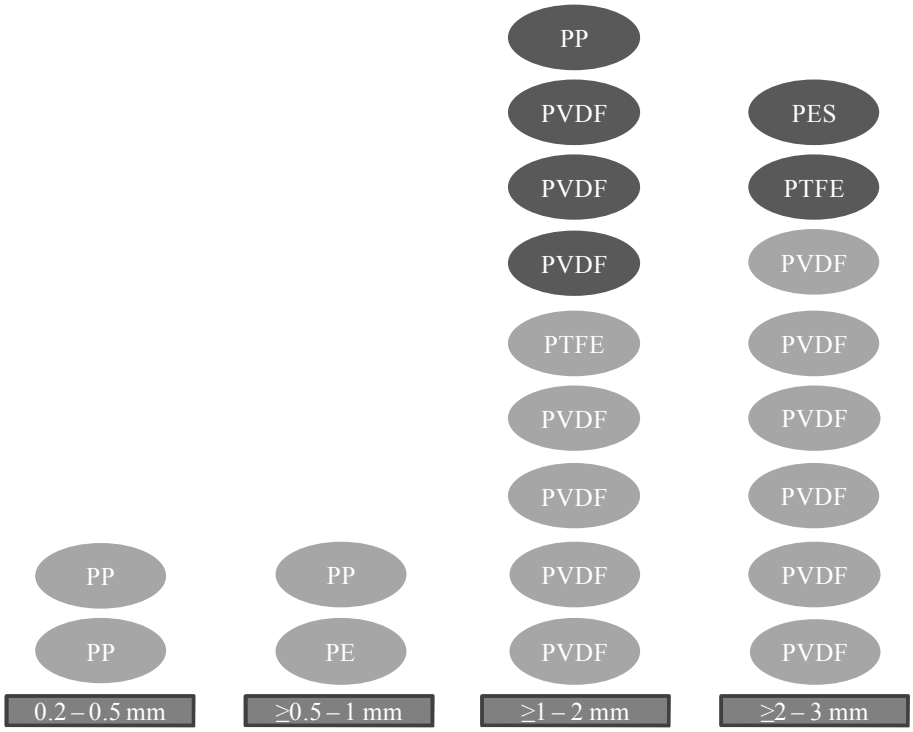

Figure 3.5 HF membrane diameters *vs* membrane material (light shadow: MF; dark shadow: UF), immersed systems

The combination of good chemical resistance and surface structure (the latter due to the wet-spinning pore formation process) has meant that the sulphonated and fluorinated polymers, and PES and PVDF in particular, dominate in modern MBR membranes. PS and PES have the widest chemical resistance, tolerating pH levels as low as 1.5 and as high as 13, as well as moderate chlorine resistance. PDVF is less tolerant of alkaline conditions, with an upper pH limit of 11, but has a very high tolerance to chlorine, which is the most widely used cleaning reagent in MBRs, and is less brittle than PES. Its chemical resistance increases with crystallinity, such that highly crystalline PVDF membranes such as the Asahi Kasei *Microza*® product have extremely high chemical resistance combined with good mechanical properties. The use of PAN and PTFE for hollow fibres is a relatively recent development, though the Orelis Pleiade® FS membrane, one of the original sidestream MBR membranes, is based on PAN.

The data for the range of fibre diameters (Figure 3.5) show that the HF MBR membranes currently range in size from 0.2 up to 3 mm. Data indicate that the polyolefinic membranes are predominantly used for smaller fibre diameter, all but one being <1 mm in fibre diameter, and are largely in the MF pore size range. For the larger-diameter fibres (>1 mm), PVDF seems to predominate.

3.3 Conclusions

The most recent available information on commercial MBR membrane technologies indicates that:

- There are approximately 45 MBR membrane product suppliers, with possibly more given that further products are close to commercialisation, 37 of them supplying immersed (iMBR) membrane modules. Given that some suppliers produce more than one product, the total number of discrete products is exceeds 50, although perhaps no more than half of these have irrefutably been demonstrated at full-scale.

- The vast majority of the iMBR products are less than 10 years old: only the Mitsubishi Rayon Engineering *SUR*®, the Zenon *Zeeweed*® and the Kubota *ES* unquestionably pre-date the year 2000. Notwithstanding the immaturity of these products, there are an increasing number of ever larger plants based on them which would appear to reflect a growing confidence in the technology *per se*, with the lead time from introduction of the technology to implementation of a large-scale plant decreasing markedly since commercialisation of the original MBR membrane products in the early 1990s.

- Around 75% of the available iMBR membrane products are either polyvinylidene difluoride (PVDF) or polyethersulfone (PES), the remainder being polysulphone (PS), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polypropylene (PP) or polyethylene (PE). The latter two materials are predominantly microfilters (>0.1 µm pore size) and of relatively small filament diameter (<1 mm) if configured as hollow fibres. The predominance of PVDF and PES reflect the desirable pore structure and chemical resistance properties of these materials.

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4 MEMBRANE BIOREACTORS: TWO DECADES OF RESEARCH AND IMPLEMENTATION

Ana Santos[1], Wenjing Ma[2] and Simon J. Judd[1]

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[1]Centre for Water Science, Cranfield University, Bedfordshire, UK
[2]Shenyang Research Institute of Chemical Industry, Shenyang, China

Abstract

Membrane bioreactor technology is widely recognised as offering a key option for enhanced wastewater treatment or reuse. This brief review of the technology incorporates four key aspects: (a) market growth, (b) research areas, (c) product supply diversity and specifications, and (d) practitioner needs. Market growth and research topics were assessed through an examination of the appropriate literature and databases, specifically *Scopus* for the latter. Available MBR membrane products were identified from internet and other searches, and the specifications verified through contact with the suppliers. Appropriate practitioners were identified through networking and verified as either being active in the operation and maintenance of full-scale MBRs or with an extensive experience of them within the industrial community. Results indicate that the footprint of modules normalised against membrane area changes significantly across the currently commercially-available product range, notwithstanding generically similar construction, such that opportunities for interchanging may be limited. The survey of research papers revealed the most comprehensively researched topic to be at odds with its practical constraints as identified by the practitioners.

4.1 Introduction

The advantages offered by membrane bioreactor (MBR) technology have been recognised for some time. An MBR comprises a conventional activated sludge process coupled with membrane separation to retain the biomass. Since the effective pore size is generally below 0.1 µm, the MBR effectively produces a clarified and substantially disinfected effluent. In addition, it concentrates up the biomass and, in doing so, reduces the necessary tank size and also increases the efficiency of the biotreatment process. MBRs thus tend to generate treated waters of higher purity with respect to dissolved constituents such as organic matter and ammonia, both of which are significantly removed by biotreatment. Moreover, by removing the requirement for biomass sedimentation, the flow rate through an MBR cannot affect product water quality through impeding solids settling, as is the case for the conventional process, although severe hydraulic and organic shock loads can be onerous in other respects.

Technological development and innovation generally is subject to drivers and barriers which ultimately determine the extent of implementation. It is widely recognised that a major driver for advancement of municipal water and wastewater treatment technology is legislation, and that two key barriers are cost and perception (Frost & Sullivan, 2003; BCC Research *et al.*, 2008). It is also the case that the scope of research associated with such development is expected to be informed by the needs of the industry, in as much as such needs are associated with the technology. For wastewater treatment technologies generally, these comprise largely generic qualities such as performance (with respect to product water quality), operational simplicity and robustness, and capital and operating costs, with costs pertaining mainly to membrane replacement and energy demand (Judd, 2008).

It has been suggested that the acknowledged high capital cost of the MBR technology can be reduced by standardisation, as exists for reverse osmosis (RO) and would allow any membrane product to be employed within an existing installation (Lesjean *et al.*, 2006; Lesjean and Huisjes, 2008; De Wilde *et al.*, 2008; Stedman, 2007). This then depends both on variation in the infrastructure and fittings required for each product and, perhaps more directly, their size. Membrane replacement costs depend on the membrane life for which data are currently scant although evidence provided from well established MBR plants (Porlock in the UK, Grand Targhee Resort in the USA and Thetis Lake Trailer Park in Canada) that a membrane life exceeding 10 years is possible. A significant contribution to energy demand is the scouring air requirement of the membrane for maintaining the membrane permeability (Verrecht *et al.*, 2008). This in turn depends on those processes which tend to reduce permeation through the membrane, normally considered to be fouling at the membrane surface (Le-Clech *et al.*, 2006; Meng *et al.*, 2009). It is these permeability reduction processes which arguably contribute most significantly to process complexity and robustness, since ameliorating strategies must be developed and imposed to reliably sustain permeability.

Notwithstanding the above barriers to implementation, the market penetration of MBR technology has been reported as growing by an average of 11.6-12.7% *per annum* since the turn of the Millennium (Srinivasan, 2007; Hanft, 2008), with this rate diminishing marginally towards 2013 (Figure 4.1). As such the MBR market has increased at rate slightly higher than that of the much larger but similarly rapidly expanding desalination membrane technologies, principally RO, for which compound annual growth rates of 9-10% have been quoted (Frost & Sullivan, 2004). In all cases, it must be assumed that the predictions do not account for the economic downturn, which may cause stagnation in the market over a period of 2-3 years (Bonnélye, 2008). However, as with desalination, the market growth in MBR technology is driven by a combination of increasing water scarcity and increasingly stringent legislation. These have tended to promote the more widespread implementation of water reuse technologies both

in the more arid regions of the world, or else made reuse more economically favourable.

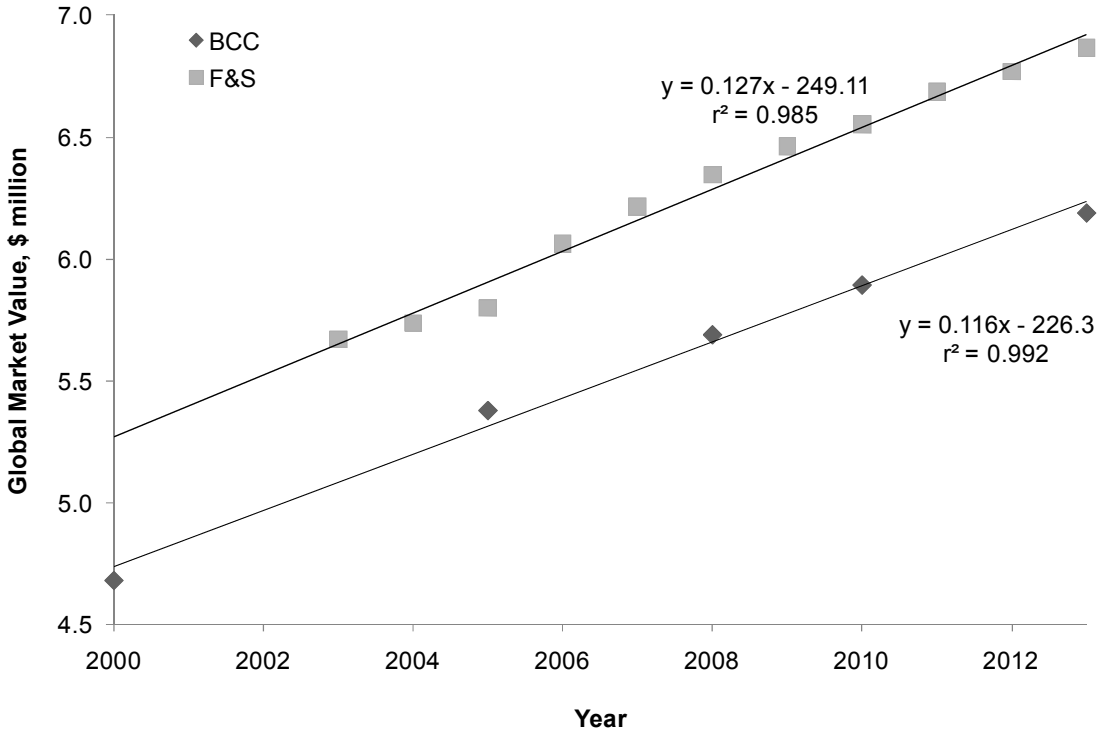

Figure 4.1 Market penetration of MBRs

Given the sustained growth in the MBR market it is of interest to establish (a) the focus of MBR research, and (b) the commercial development of MBR technologies as pertaining to the recognised needs of the industry. In the current study this was approached through individual surveys of (i) the peer-reviewed scientific/technical literature, (ii) the current MBR products, and (iii) practitioners. The surveys of the literature and technologies were designed to establish the respective rate of increase in the number of (i) publications in key research topics, and (ii) MBR membrane module products. In the case of the latter, a review of the individual product specifications allows their interchangeability to be assessed through calculation of the membrane module footprint imposed for a given membrane module area. Information from (i) and

(ii) could then be assessed on the basis of the review of the practitioners and the technological challenges as perceived by them.

4.2 Methodology

The work comprised a series of surveys conducted between December 2009 and March 2010.

4.2.1 Research survey

A search on literature on MBR for wastewater treatment published between 1990 until 2009 was carried out using the search engine *Scopus* (www.Scopus.com). The survey was conducted based on the research terms identified in Table 4.1 so as to identify, first through a blind search, those papers dedicated to specific topics or subject areas, namely:

1. Fouling of the membrane surface
2. Clogging of the membrane channels
3. Individual configurations
4. Hybrid processes
5. Micropollutants
6. Screening

These terms were selected on the basis of their relative reflection of key drivers and impacts, given:

- the relative importance of the three MBR membrane configurations in the market place

- the high profile attained by micropollutants, such as endocrine disrupting compounds, promoted by the implementation of the Water Framework Directive 2000/60/EC (WFD) (European Commission, 2000),

- the increasing importance of hybrid processes, specifically intended to reduce the energy demand exerted by the benchmark MBR-RO process employed for water reuse.

Table 4.1 Terms employed for the database search

Primary terms	Secondary terms (taken from 1-6)
"MBR" **OR** **"Membrane bioreactor"** **OR** **"Membrane separation bioreactor"** **OR** **"Membrane biological reactor"** **AND** **("Wastewater" OR "Sewage")**	1. "Fouling" OR "Biofouling" 2. "Clogging" OR "Sludging" 3a. "Hollow fibre" OR "Hollow fiber" 3b. "Flat sheet" OR "Flat plate" OR "Plate and frame" 3c. "Tubular" OR "Multi tube" 4. "Nanofiltration" OR "MBR-NF" OR "Membrane distillation" OR "MD" OR "Forward osmosis" OR "FO" 5. "Micropollutants" OR "Endocrine disrupting compounds" OR "EDC" OR "Pharmaceutical" OR "Personal care products" OR "PCP" 6. "Screening"

The search terms were applied to the titles and the keywords. Abstracts from the individual papers identified from the blind search were then individually examined to establish whether the term identified was subject to investigation within the actual paper. Titles and keywords of the relevant papers were then listed in a single spreadsheet and subject to further analysis, either through summing the number of papers within the individual categories indicated in 1-6 or else through the production of a "word cloud" (www.wordle.net), which provides a graphic in which the frequency at which words arise is indicated by the font size. For the word cloud analysis it was necessary to correct all spelling

to UK English and exclude common words and their plurals. These words were excluded on the basis that of them being generic terms for (a) MBR studies, and (b) scientific studies generally, and are listed below:

- Generic technical terms for MBR studies (and their plurals): Activated sludge, Bioreactor, Biological, Filtration, Liquor, MBR, Membrane, Mixed, Products, Reactor, Retention, Separation, Substances, Technology, Treatment, Wastewater.

- Generic terms for scientific studies (and their plurals): Activity, Analysis, Application, Comparison, Effect, Evaluation, Impact, Influence, Investigation, Performance, Research, Study, Activity, Based, Characteristics, Compounds, Concentration, Conditions, Different, Factors, High, Low, New, Novel, Operation, Operational, Plants, Process, Production, Properties, Removal, Size, Specific, Structure, System, Time, Transfer, Treating, Using.

4.2.2 Membrane module product suppliers survey

The commercial MBR membrane products identified were as outlined in a previous review (Chapter 3) through searches of the internet, technical ("grey") literature, business networking sites and general active networking. Product specifications were verified through contact with the suppliers for the 45 individual products identified (Table 4.2) and were used to calculate two key parameters relating to standardisation:

A_m:F – The unitless ratio of the membrane area A_m to the footprint F, where F is the cross-sectional area at the module base

φ – The module packing density, or the membrane area *per* unit module volume in m^{-1}; this equates to the A_m:F ratio divided by the module height.

The distribution in values of the above two parameters was then used to assess the extent to which the modules could be interchanged, assuming this to be constrained primarily by space occupation. As an adjunct to the market analysis data shown in Figure 4.1, the rate of introduction of the commercial products to the market was also assessed.

Table 4.2 Total MBR technologies reviewed

Flat sheet (FS) – 20 products	Hollow fibre (HF) – 25 products
A3 – MaxFlow DE	Asahi Kasei – Microzoa® JP
Alfa Laval – Hollow Sheet SE	Beijing EDI – Canfil CN
Brightwater – MEMBRIGHT® IRL	Beijing Origin Water Technology – BSY/RF CN
Colloide – SubSnake NIR	Ecologix – EcoFlon™, EcoFil CN
Ecologix – EcoPlate™, EcoSepro CN	ENE – SuperMAK KR
Huber – VRM®; VUM®/GreyUse DE	GE Zenon – ZeeWeed® NA
Hyflux – Petaflex SG	Hangzhou H-Filtration – MR CN
Jiangsu Lantian Peier Membrane CN	Koch Membrane Systems – Puron® NA
LG/KOReD – Green Membrane KR	Korean Membrane Systems – KSMBR® KR
Kubota – ES/EK JP	Litree – LH3 CN
MICRODYN-NADIR – BioCel® DE	Memos – MEMSUB DE
Pure Envitech – ENVIS KR	Memstar – SMM SG
Toray – TRM JP	Micronet Porous Fibers – Micronet® SP
Shanghai Megavision CN	Mitsubishi Rayon – Sterapore SUR®; SADF® JP
Shanghai SINAP CN	Philos KR
Vina Filter – Vinap CN	SENUO Filtration Technology – SENUOFIL CN
Weise – MicroClear® DE	Shanghai Dehong CN
	Siemens Water Technology – MemPulse™ DE
	Sumitomo – PoreFlon® JP
	Superstring MBR Technology – SuperUF CN
	Tianjin Motimo – FP AIV CN
	Vina Filter – F08 CN
	Zena Membranes – P5 CZ

CN: China/Taiwan; CZ: Czech Republic; DE: Germany; IRL: Southern Ireland; JP: Japan; KR: Korea; NA: North America (USA/Canada); NIR: Northern Ireland; SE: Sweden; SG: Singapore; SP: Spain

4.2.3 Practitioner survey

The survey of practitioners took the form of a single question to a range of 65 stakeholders identified as membrane product suppliers, technology suppliers, end users, and consultants, with inevitably some overlap arising between these broad categories. Selection was on the basis of demonstrated direct or experience of the design and/or operation and maintenance of membrane bioreactor technology at full-scale, and was largely directed at municipal wastewater practitioners. The survey comprised a single question, this being:

What is the main technical problem that prevents MBRs working as they should?

It was stipulated that the term “technical” should exclude human and logistical issues, such as operator training/engagement and supply chain management, but could include anything relating to design and O&M. Responses were collated under a number of general categories.

4.3 Results

4.3.1 Research publications analysis

4.3.1.1 Word cloud

Word clouds generated from the most frequently used in the source titles and keywords are shown in Figure 4.2 and Figure 4.3 respectively from the 1449 number of papers identified as concerning membrane bioreactors. The analysis was restricted to the 30 most frequently used words. Whilst the most common words are differently sized between the two different sets of analysis, it is evident that most MBR research papers concern membrane fouling in immersed systems, with a focus on extracellular polymeric substances (EPS) and soluble microbial products (SMP). Some terms common to both clouds are generic to membrane technology, *e.g*. microfiltration and ultrafiltration, but it is

noticeable that term “hollow fibre” is common to both whereas “flat sheet” arises in neither. Other terms common to both clouds include generic biotreatment terms like “nitrification”, “organic”, “aeration”, “aerobic” and “anaerobic”, with the latter somewhat surprisingly marginally more common that the “aerobic” term. There is obvious a stronger focus on municipal and domestic wastewater sources than industrial ones, and the appearance of the terms “phosphorus”, “nitrogen” and “denitrification” reflects an expected emphasis on nutrient removal. Aeration for membrane scouring represents a key topic in MBR research, since this has a significant impact on the overall process energy demand.

Figure 4.2 Word cloud produced from MBR research paper titles

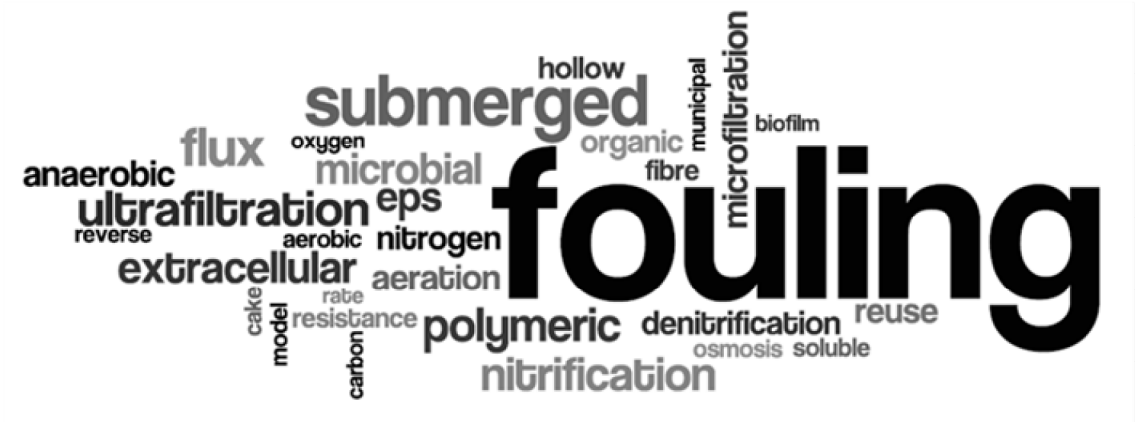

Figure 4.3 Word cloud produced from MBR research paper keywords

4.3.1.2 Analysis by subject area

A word cloud does not necessarily illustrate a trend but rather provides an overall visual impression through identification of the most frequently used words in piece of text. Quantitative analysis of the *Scopus* database through summing the total number of papers devoted to specific topics on an annual basis (Figure 4.4) indicates the growth of papers published in these areas, with the number research publications in MBRs overall apparently having increased at a steady exponential rate of 20% year-on-year between 1995 and the end of 2009.

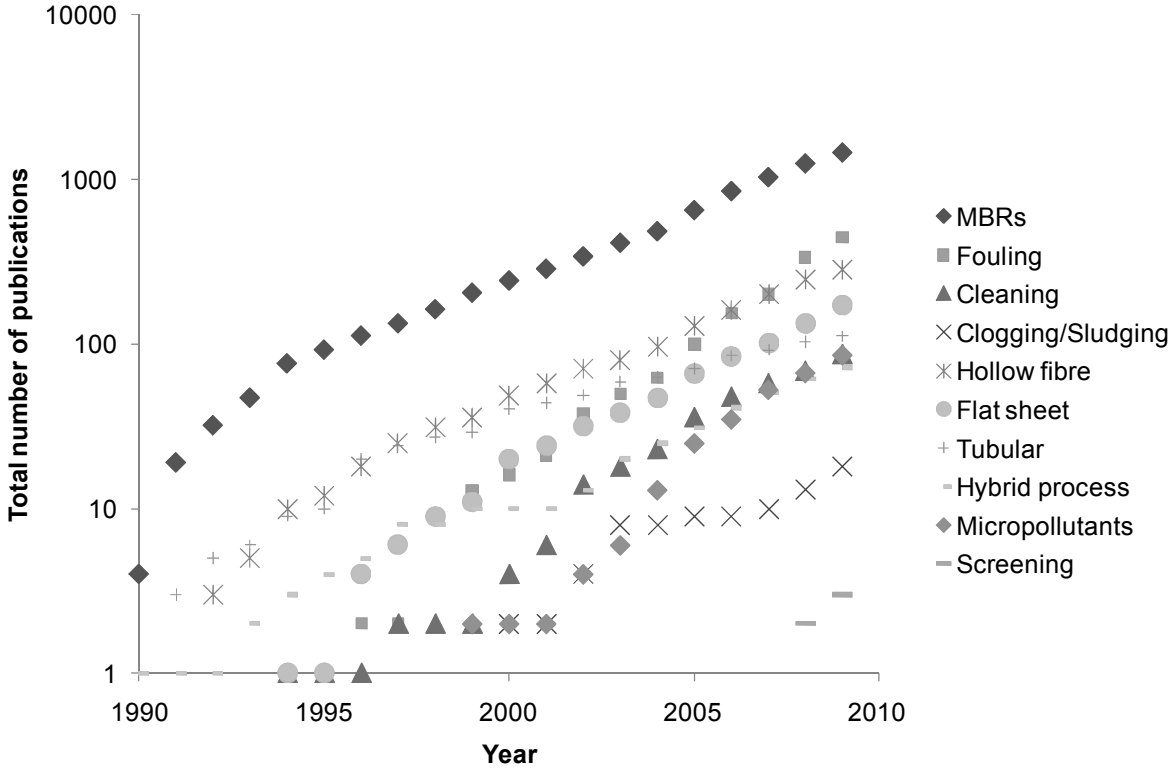

Figure 4.4 Research trends in MBRs: number of publications in key subject areas according to *Scopus*

It is apparent from Figure 4.4 that, following an indeterminate initial period, all but one of the research topics identified under the areas listed in 1-6 in section 4.2.1 follows an exponential trend with an r^2 of at least 0.96. These trends from Figure 4.4 are summarised in Table 4.3. It is evident from these data that, whilst the number of MBR papers has been increasing by around 20% year-on-year since 1995, specific topics within the general subject area of MBRs have generally been increasing at an appreciably faster rate. Of these the most noteworthy are fouling, for which the number of publications have increased by 36% year-on-year and currently make up around 31% of all MBR publications, and micropollutants. The latter trend is less poorly defined, but the rapid growth in publications is clearly driven by legislation and its impact on the environment (Rowsell *et al.*, 2010; Corvini and Shahgaldian, 2010; Kimura *et al.*, 2009; Miège *et al.*, 2009). Similarly, the resurgence of interest in hybrid processes, *i.e*. MBRs combined with nanofiltration, forward osmosis and membrane distillation, that has led to a 21% year-on-year increase in publications since 2001 has been driven largely by increasing concerns over the energy usage of MBRs. The split between hollow fibre (HF), flat sheet (FS) and tubular (Tu) papers roughly reflects the market penetration of these three configurations, with the HF configuration forming the basis of about 60% more studies than that of the FS one although increasing at a slightly slower rate. Against these well defined trends, there are an insignificant number of publications in MBR membrane clogging (or sludging), and screening, with no clear trend (r^2=0.87) in the case of clogging.

Table 4.3 Research and market trends

Research topic	Start date [a]	Increase *per annum*, %	r^2	Total at end 2009
MBRs	1995	20	1.00	1449
Fouling	1998	36	1.00	446
Cleaning	2002	27	0.98	87
Clogging/Sludging	2000	23	0.87	18
Hollow fibre (HF)	1996	21	1.00	283
Flat sheet (FS)	1999	26	0.99	173
Tubular (Tu)	1996	13	0.99	112
Hybrid process	2001	21	0.99	72
Micropollutants	2002	45	0.96	86
Screening	2008	41	1.00	3
Market value, F&S [b]	2003	13	0.98	700
Market value, BCC [b]	2000	12	0.99	363

r^2: Coefficient of determination; [a]Start of defined exponential trend in Figure 4; [b]Taken from Figure 4.1

4.3.2 MBR membrane product assessment

The A_m:F ratio and φ values of the products listed in Table 4.2 are depicted in Figure 4.5 and Figure 4.6, respectively, which categorise the two configurations (FS and HF) according to:

- the number of decks of flat sheet modules (1-3), and
- the geometry of the bundles/elements of hollow fibres in a module.

FS stacks are normally either single or double deck, though if the individual panel of which the module is comprised is sufficiently short then it is possible to fit a triple deck within the membrane tank, which is not normally more than 5 m deep. HF systems may be comprised of either rectangular elements, which are then placed in a cassette in an analogous fashion to the FS panels, or else formed into cylindrical bundles which form an array within the stack. HF systems are normally single deck, though there are 2-3 which are stackable and for these the largest stack was selected.

Figure 4.5 and Figure 4.6 show a broad range of both A_m:F ratio and φ values across the range of products, with higher values for the HF products (Table 4.4). Figure 4.7 and Figure 4.8 show the MBR product suppliers split by four main groups: leading market established companies, established international companies, early stage international suppliers and others.

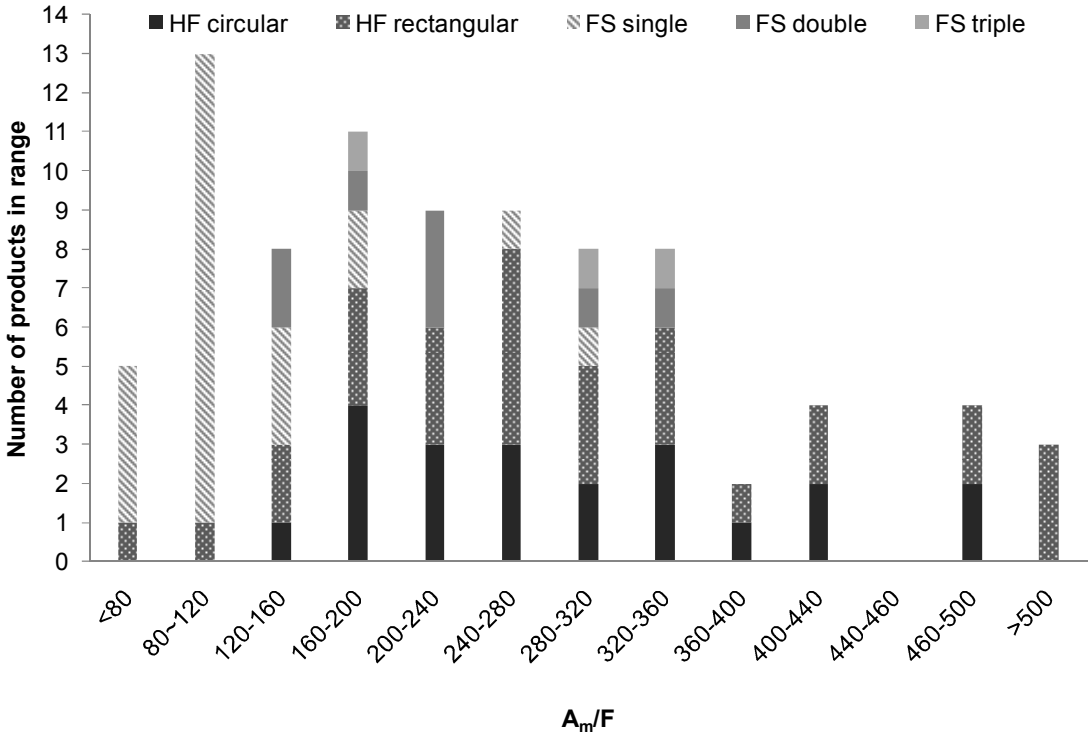

Figure 4.5 Number of products against ranges of membrane area to module footprint ratio (A_m:F) values

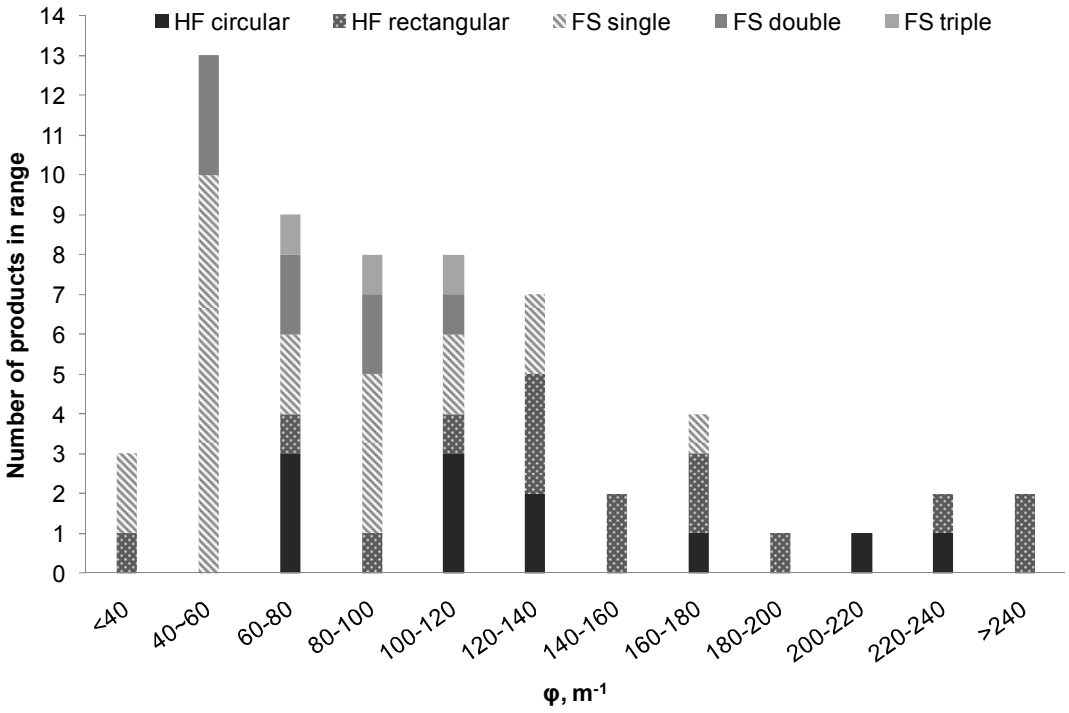

Figure 4.6 Number of products against ranges of packing density (φ) values

Table 4.4 Summary of module product parameters

		A_m/F single	*A_m/F double*	*Packing density, φ*
FS	Mean	118	217	77
	SD	58 (49%)	67 (31%)	31 (41%)
HF	Mean	292		141
	SD	119 (41%)		67 (48%)

Most FS panels are 4-7 mm in thickness (t), with the exception of some of the newer ultrathin modules, and generally separated by 6-8 mm (δ) in the stack. This means that the maximum possible packing density – the panel packing density φ_{panel} – for an FS stack is given by (Judd and Judd, 2006):

$$\varphi_{\text{panel}} = \frac{2000}{(\text{t} + \delta)} \quad \textbf{(4.1)}$$

According to this correlation, and based on the specifications provided for the FS modules listed in Table 4.2, φ_{panel} across the range of products is between 125 and 267 m^2 m^{-3}. It might then be expected for φ_{panel} to correlate with the packing density of the module (φ). However, this does not appear to be the case (Figure 4.7). The plot indicates that 76% of the products have φ_{panel} values in the 130-160 m^2 m^{-3} range, whereas the corresponding φ values are between 30 and 130 m^2 m^{-3} with the two market leader supplier products ending to be placed at the lower range – *i.e*. with relatively low packing densities.

In the case of the HF products, where filament diameters vary between 0.2 and 3 mm across the entire range, it may again be expected for the packing density to increase with decreasing fibre diameter. As with the FS products, there is no evident correlation (Figure 4.8), with a wide range of packing densities (from 40 to 250 m^2 m^{-3}) arising from a very narrow range of fibre size (1.2-1.3 mm) representing almost half of the 25 products presented. In this case the most established products are not readily distinguishable from the others.

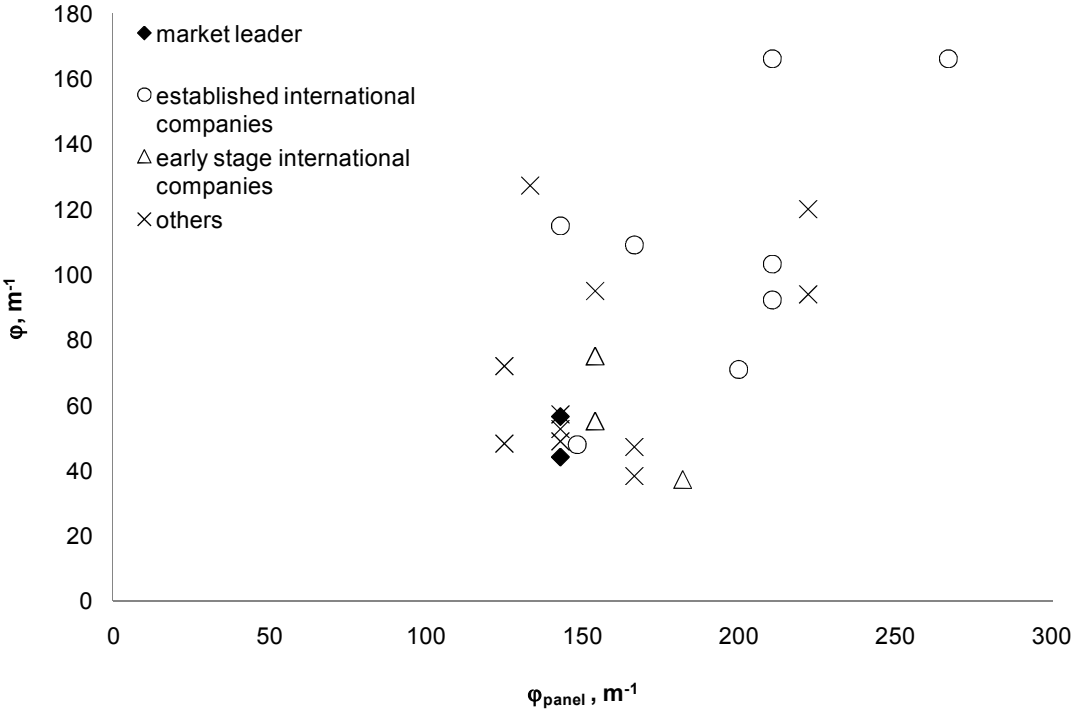

Figure 4.7 Module packing density (φ) *vs* panel packing density (φ_{panel})

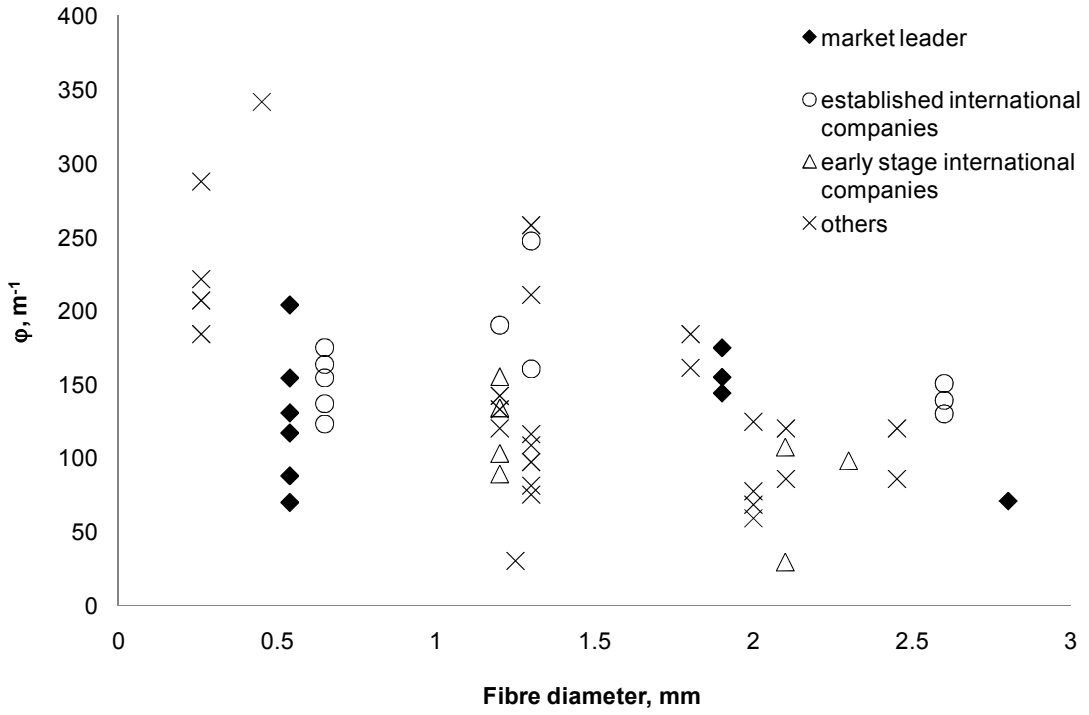

Figure 4.8 Number of products against ranges of packing density (φ) values

4.3.3 Practitioner survey

Of the 65 practitioners surveyed, 48 (74%) responded. Of these 48, one response was too aspecific to permit categorisation. Two further responses identified a subject which was specifically identified as being invalid in the survey questionnaire (operator knowledge), but were none-the-less included in the analysis. The split between nationalities of the respondents was 23% US: 64% Europe: 13% Asia/Australia, and that between vocation 17% end user, 33% consultant, 27% technology or process supplier and 23% MBR membrane product supplier. The academic profession was specifically excluded from the survey. Of the respondents, 12 provided more than one answer. In these cases, a weighting of 0.5 was applied to each answer for two answers or 0.33 for three.

Analysis of the responses revealed that they fell broadly into ten categories (Figure 4.9), with obvious inter-relationships between some of these. The top

two rated responses, at 22 and 19%, respectively related to (i) pre-treatment and screening, and (ii) membrane and aerator clogging. These two responses were followed by issues relating to (iii) hydraulic overloading or system under design (17%), and then (iv) membrane fouling or fouling resistance (15%). Given that the most direct consequence of poor screening is clogging by gross suspended solids ("sludging"), there is an obvious causal relationship between these two issues. Similarly, the most immediate impact of overloading is membrane fouling, and irreversible membrane fouling necessitates cleaning; it was noticeable that the industrial effluent treatment practitioners tended to identify fouling as the key issue. Notwithstanding this, the aggregate percentage value of the number of responses pertaining to fouling, cleaning and overloading is 38% – less than the aggregate value for clogging and screening (41%).

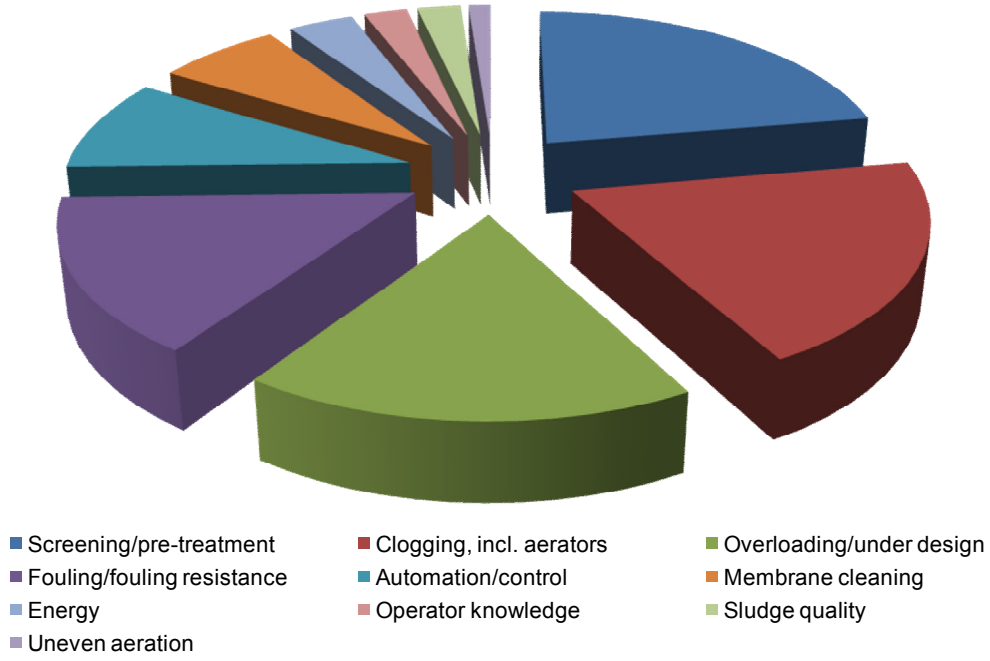

Figure 4.9 Analysis of topics identified from the practitioner survey (48 respondents)

4.4 Conclusions

Research publications on membrane bioreactors are growing in number exponentially at a rate of 20%, compared with a commercial growth rate of 11-13%. Analysis of the topics forming the focus of the research into MBRs reveals that publications concerning membrane fouling, particularly with reference to extracellular polymeric substances, is the most prominent of all those appraised and growing at faster rate than all but one of the topics considered. Only published studies of micropollutants are growing faster, this obviously being promoted by legislation. Fouling papers currently accounted for around 31% of all MBR papers published, as opposed to 1% for papers on clogging (which have been mainly anecdotal in nature) and an insignificant number on screening.

The focus on fouling would appear to be at odds with the process challenges as identified by a survey of practitioners, where screening and clogging were found to be of most concern and fouling only considered as being the most important issue by 15% of the respondents. Whilst the survey was somewhat based towards municipal wastewater practitioners, the majority of the publications on fouling characterisation are based on the treatment of municipal wastewater.

Specification data from across the entire range of MBR module products suggest that interchangeability between products may be limited. Differences in the overall design of the stacks/cassettes/units means that the volume they occupy *per* unit area of membrane differs appreciably across the whole product range. This analysis takes no account of the required spacing between the modules in the tank, and also ignores other practical issues such as connections and their positioning on the modules. The range of space occupation of the products is surprising given that the generic design – particularly for the flat sheet membrane modules – is ostensibly the same across the whole range.

It appears that, whilst market penetration of MBR technology is significant, there is much to address in advancing the cause of MBRs commercially. Whilst membrane fouling is a generic limitation of membrane processes, it is not perceived the primary constraint on effective operation of the MBR process. Also, whilst there has been much interest in standardisation over the past few years, a simple survey of specifications of existing products suggests that there are wide variations in their spatial occupancy which would be expected to mitigate against interchangeability.

Acknowledgements

The authors are very grateful to the 48 practitioners taking part in the survey.

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5 FATE AND BEHAVIOUR OF COPPER AND ZINC IN SECONDARY BIOLOGICAL WASTEWATER TREATMENT PROCESSES: II REMOVAL AT VARYING SLUDGE AGE

Ana Santos[1], Paul Barton[1], Elise Cartmell[1], Frederic Coulon[2], Richard S. Crane[3], Peter Hillis[4], John N. Lester[1], Tom Stephenson[1] and Simon J. Judd[1]

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[1]Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK
[2]Centre for Resource Management and Efficiency, Cranfield University, MK43 0AL, UK
[3]Integrated Alliance, Great Sankey, Warrington, Cheshire, WA5 3LP, UK
[4]United Utilities, Great Sankey, Warrington, Cheshire, WA5 3LP, UK

Abstract

The mechanisms for the removal of heavy metals during secondary biological treatment of wastewater with particular emphasis on the activated sludge process are considered. It is concluded that the predominant mechanism is the entrapment and co-settlement of insoluble metal species in the mixed liquor (biomass). Secondarily extracellular polymeric materials particularly extracellular polysaccharides and other capsule forming materials may also play a role. In general removal of both copper and zinc was superior at the higher sludge ages employed in this study 4.3 and 8 days and can in part be attributed to the superior removals of both Biochemical Oxygen Demand and effluent suspended solids achieved at these sludge ages as opposed to the lowest sludge age studied 3.6 days. For both copper and zinc there is an increase in soluble metal across the activated sludge process. However, significant removal of both metals occurs as a consequence of the removal of substantial amounts of insoluble metal. The presence of return sludge liquors high in settleable solids to the mixed liquor appears to moderately enhance the percentage removal of copper and zinc. Membranes used in place of secondary

sedimentation also enhance removal of both metals by reducing effluent suspended solids. It is concluded that there is potential for maximizing metal removal by optimization of secondary biological treatment in a sustainable manner, without recourse to energy intensive or chemically dependent tertiary treatment technologies.

5.1 Introduction

Certain metallic elements are potentially hazardous to the aquatic environment (cadmium, copper, chromium, lead, mercury, nickel and zinc) and these have been identified by the United States Environmental Protection Agency (USEPA) as priority toxic pollutants (US EPA, 2006). The European Union (EU) has designated cadmium, lead, mercury and nickel as priority substances under the Water Framework Directive (2000/60/EC) whilst copper, chromium and zinc are designated as potential main pollutants (European Commission, 2000). Additional legislation and detailed descriptions of criteria and values pertaining to these elements have recently been summarised and reviewed (Ziolko *et al.*, 2010; Brown and Lester, 1979).

Copper and zinc are two of the most abundant metallic elements in crude sewages and although not intended to conventional wastewater treatment significantly reduces the concentrations of both elements in final effluents (Ziolko *et al.*, 2010; Brown and Lester, 1979; Lester, 1983; Sterritt and Lester, 1984b; Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Roberts *et al.*, 1977). The reductions in the quantities of these elements entering crude sewage over the past 25 years (Crane *et al.*, 2010 – Appendix A) coupled to the substantial degrees of removal achieved in conventional two stage sewage treatment works (Brown *et al.*, 1973; Oliver and Cosgrove, 1974; Lester *et al.*, 1979; Stoveland *et al.*, 1979; Goldstone *et al.*, 1990b Goldstone *et al.*, 1990c) had been deemed to afford adequate protection of the aquatic environment. Reappraisal of environmental impacts of these elements in the hydrosphere has resulted in new legislation in both the United States of America where new Water Quality Criteria have been set as amendments to the Clean Water Act (1970) by the US EPA (2006) and in Europe where new Environmental Quality Standards have been established and incorporated into legislation at the national level (UK TAG, 2007). Whilst there are variations between the two continents and actual values are affected by consideration of water hardness (Table 5.1) the actual values set for copper in freshwater water are in the range 6-9 µg l^{-1} and for zinc 50-120 µg l^{-1} (Ziolko *et al.*, 2010). These developments

have resulted in the requirement to establish the concentration and quantities of toxic metals including copper and zinc entering wastewater treatment works, their removals and concentrations in final effluents and hence the contribution they make to concentrations observed in surface waters receiving sewage effluents (Ziolko *et al.*, 2009).

Table 5.1 Current metal standards for copper and zinc (Ziolko *et al.*, 2010)

	Freshwater			Estuarine			HHC
Metal	EQS (EA)	CMC (US EPA)	CCC (US EPA)	EQS (EA)	CMC (US EPA)	CCC (US EPA)	Water and Dissolved Metal (US EPA)
Cu, $\mu g\ l^{-1}$	6	13	9	5	4.8	3.1	1300
Zn, $\mu g\ l^{-1}$	50	120	120	40	90	81	7400

EQS: Environment Quality Standard; CMC: Criteria Maximum Concentration; CCC: Criteria Continuous Concentration; EA: Environment Agency of England and Wales; US EPA: United States Environmental Protection Agency; HHC: Human Health for Consumption of.

Secondary biological wastewater treatment is paramount in attaining the final effluent heavy metal concentrations now observed (Lester *et al.*, 1979; Ziolko *et al.*, 2009; Stoveland and Lester, 1980; Sterritt and Lester, 1981; Sterritt *et al.*, 1981; Sterritt and Lester, 1982; Rossin *et al.*, 1982; Kempton *et al.*, 1983; Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c; Lawson *et al.*, 1984d; Rudd *et al.*, 1984a; Stephenson and Lester, 1987a; Stephenson and Lester, 1987b; Stephenson *et al.*, 1987; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Buzier *et al.*, 2006; Fatone *et al.*, 2006; Fatone *et al.*, 2008; Innocenti *et al.*, 2002; Mansell *et al.*, 2004; Scrimshaw, 2009; Cecchi *et al.*, 2003) which are required to achieve the current Environmental Quality Standards shown in Table 5.1 (Ziolko *et al.*, 2010). Removal of heavy metals during biological treatment is a complex process and only the activated sludge process has been studied in depth (Brown and Lester, 1979; Lester, 1983; Lester, 1987), but the same processes are assumed to operate in other biological secondary treatment processes *e.g*. trickling (or percolating) filters

(Lester, 1987) and membrane bioreactors (MBRs) (Table 5.2). In the activated sludge process the removals for copper vary from 25-94% and for zinc 30-79%. Whilst for MBRs copper removal varied from 64-94% and zinc removal from 26-94%. In trickling filters (TF) the equivalent figures were 22-66% for copper and 80% (one value reported) for zinc. It may generally be concluded that the removals for activated sludge and MBRs were broadly similar whilst those for copper in trickling filters were inferior to activated sludge plants (ASP) and MBRs.

Table 5.2 Reported copper and zinc removal rates by activated sludge, trickling filter and MBR plants

			Total Copper		Total Zinc		
Scale	HRT, hrs	SRT, d	Conc., µg l^{-1}	% Removal	Conc., µg l^{-1}	% Removal	Reference
Activated Sludge Plant							
FS	-	-	40	86	420	78	Lester *et al.*, 1979
PS	-	-	98	43	530	57	Davis III and Jacknow, 1975
FS	-	-	79	58	470	43	Karvelas *et al.*, 2003
FS	-	2	35	57	-	-	Buzier *et al.*, 2006
FS	-	-	56	55	-	-	Fatone *et al.*, 2008
PS	6-8	40-60	43	79	427	66	Fatone *et al.*, 2006
FS	-	10-13	40	94	445	79	Ziolko *et al.*, 2009
FS			72	25	390	30	Roberts *et al.*, 1977
MBR							
PS	14	11->1000	56	72-89	-	-	Fatone *et al.*, 2008
PS	14	190	-	72-89	-	56	Innocenti *et al.*, 2002
PS	6-8	40-60	43	95	427	94	Innocenti *et al.*, 2002
PS	-	10-20	-	80-81	-	37-26	Mansell *et al.*, 2004
BS	-	30-50	-	64-94	-	-	Cecchi *et al.*, 2003
PS	14	190->300	53	79-90	274	51-94	Cecchi *et al.*, 2003
Trickling Filter							
FS			13	22	-	-	Ziolko *et al.*, 2009
FS			18	52	-	-	Ziolko *et al.*, 2009
FS			28	71	-	-	Ziolko *et al.*, 2009
FS			112	50	-	-	Ziolko *et al.*, 2009
FS			19	55	-	-	Ziolko *et al.*, 2009
FS			20	52	-	-	Ziolko *et al.*, 2009
FS			16	66	-	-	Ziolko *et al.*, 2009
FS					445	80	Scrimshaw, 2009

BS: Bench Scale; PS: Pilot-scale; FS: Full-scale; (-) not specified

The mechanisms proposed by Brown and Lester for the removal of dissolved and fine particulate metals in the activated sludge process include the following (Brown and Lester, 1979):

1. Physical trapping of precipitated metals in the sludge floc matrix;
2. Binding of soluble metal to extracellular polymers;
3. Accumulation of soluble metal by the cell; and
4. Volatilization of metal to atmosphere.

The elucidation of these mechanisms and their relevant importance has been achieved by the study of full-scale wastewater treatment works (Roberts *et al.*, 1977; Lester *et al.*, 1979; Stoveland *et al.*, 1979; Goldstone *et al.*, 1990c; Ziolko *et al.*, 2009; Karvelas *et al.*, 2003; Buzier *et al.*, 2006; Fatone *et al.*, 2008; Scrimshaw, 2009; Goldstone *et al.*, 1990b; Goldstone *et al.*, 1990a) pilot plants (Rossin *et al.*, 1982; Stephenson and Lester, 1987a; Stephenson and Lester, 1987b; Davis III and Jacknow, 1975; Fatone *et al.*, 2006; Fatone *et al.*, 2008; Innocenti *et al.*, 2002; Mansell *et al.*, 2004; Cecchi *et al.*, 2003; Rossin *et al.*, 1983; Kempton *et al.*, 1987a; Kempton *et al.*, 1987b) laboratory scale simulations (Rossin *et al.*, 1982; Stoveland and Lester, 1980; Sterritt and Lester, 1981; Sterritt *et al.*, 1981; Sterritt and Lester, 1982; Kempton *et al.*, 1983; Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c; Lawson *et al.*, 1984d; Stephenson *et al.*, 1987; Cecchi *et al.*, 2003; Sterritt and Lester, 1980b; Brown and Lester, 1982a; Brown and Lester, 1982b) and batch studies or “jar-tests” (Stoveland and Lester, 1980; Kempton *et al.*, 1983; Rudd *et al.*, 1984a; Rudd *et al.*, 1983b; Rudd *et al.*, 1984b; Sterritt and Lester, 1984a; Sterritt and Lester, 1985; Rudd *et al.*, 1988).

Volatilization is feasible in the case of those elements which are biotransformable to organo-metallic species *via* methylation *e.g.* arsenic, mercury, lead, tellurium, selenium (Goldstone *et al.*, 1990a). Whilst the methylation of mercury may occur during aerobic activated sludge treatment (probably deep within the flocs which are either microaerophillic or anoxic)

however, the extent is extremely limited probably <1% (Goldstone *et al.*, 1990a) and as methyl mercury is not particularly volatile losses *via* this pathway are neglible. It is possible tellurium can be methylated as a strong smell of garlic (dimethyl tellurite) emanated from laboratory scale activated sludge simulations to which an inorganic tellurium salt was introduced (Kempton *et al.*, 1983). However, mass balances of the phases within the system indicate that there is a very small amount of this volatile species produced (Kempton *et al.*, 1983). Whilst some elements *e.g*. tin can enter wastewater treatment works in an organo-metallic form *e.g.* tributyl tin oxide (Voulvoulis *et al.*, 2004) it is not volatile (Dowson *et al.*, 1993) and mass balances demonstrate it is not lost *via* that route (Voulvoulis *et al.*, 2004; Voulvoulis and Lester, 2006).

Accumulation of metal within the cells of activated sludge bacteria either by active or passive uptake is also thought to be a minor mechanism for metal removal in the activated sludge process (Lamb and Tollefson, 1973; Patrick and Loutit, 1976). The extent of intracellular accumulation maybe dependent on sludge age with higher sludge ages generally enhancing accumulation (Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Uloth and Mavinic, 1977) and this has been observed in pure cultures of *Klebsiella aerogenes* grown in continuous culture where the uptake of cadmium and copper were examined (Rudd *et al.*, 1983a). Studies of active uptake and passive uptake of metal were made by Lawson *et al.* (1984c) using activated sludge deactivated with formaldehyde, to distinguish between active uptake into the cell and passive adsorption to extracellular polymeric materials (EPM) and the cell surface. It was reported that the active biomass exhibited greater uptake of copper and nickel whereas cadmium exhibited greater uptake by the inactivated biomass. Following the additional observation that bulking sludge adsorbed more metal than a well flocculating biomass, it was concluded that the structure and function of the activated sludge were of more importance in metal removal than its viability (Rudd *et al.*, 1983a).

The role of bacterial extracellular polymers in metal removal has been extensively studied (Brown and Lester, 1979; Brown and Lester, 1982a; Brown and Lester, 1982b; Uloth and Mavinic, 1977; Wilkinson, 1958; Sutherland, 1972; Corpe, 1975; Novak *et al.*, 1977) the polysaccharides secreted by the bacteria contain additional proteins, nucleic acids and other products of cell lysis in the activated sludge process. This extracellular capsular material may play a significant role in the removal of soluble copper and cadmium and to a lesser extent nickel, depending on operating conditions (Brown and Lester, 1982a). Sludge age/solid retention time (SRT) may be of particular importance in this respect (Brown and Lester, 1982b).

The entrapment and settlement of particulate non-settleable metal containing solids however is the most important mechanism of metal removal in the activated sludge process (Sterritt and Lester, 1981; Kempton *et al.*, 1983; Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c; Lawson *et al.*, 1984d; Stephenson *et al.*, 1987; Cheng *et al.*, 1975; Chen *et al.*, 1974). This has been clearly established by a series of elegant batch studies conducted by Stephenson *et al.* (1987a; 1987b). Batch studies have also be used to determine the absorptive capacity of various biological sludges to access their potential for metal removal (Sterritt *et al.*, 1981; Rudd *et al.*, 1984a; Rudd *et al.*, 1983b; Rudd *et al.*, 1984b).

The aim of this study was to assess the role of SRT on the removal of copper and zinc during activated sludge treatment and to determine the impact of return liquors on metal removal. In addition the potential of membranes to achieve final phase separation was examined to establish if they could provide a means to enhance overall metal removal thus minimising final effluent copper and zinc concentrations.

5.2 Materials and methods

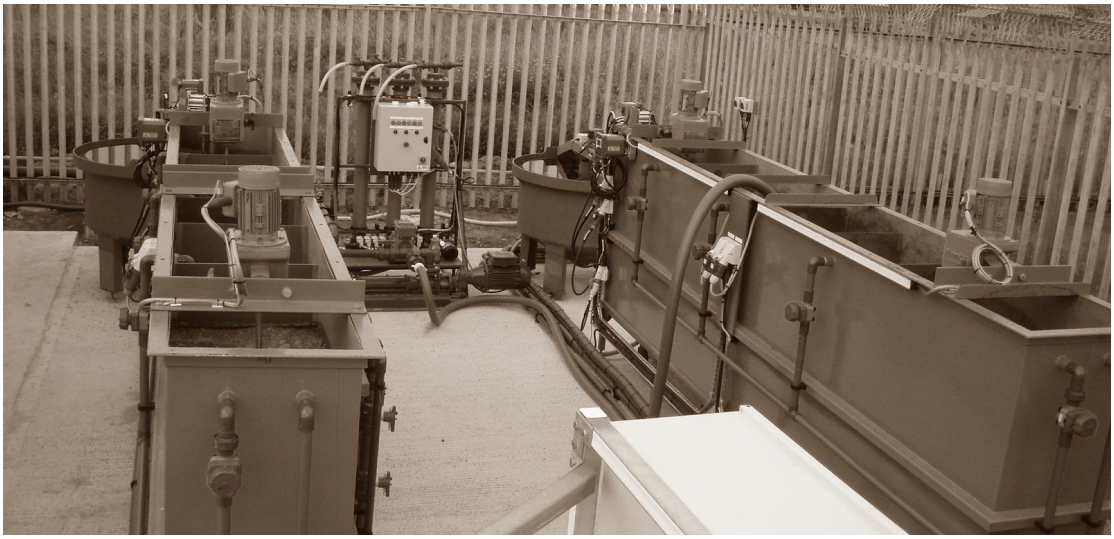
5.2.1 Activated sludge pilot plant

Experiments were conducted using an activated sludge pilot plant over a period of 13 weeks at a wastewater treatment works in the North West of the UK with a population equivalent (p.e.) of 140,365. The wastewater treatment works (WwTW) was fed by two inlets; the 'high' level and 'low' level sewers. Sewage entering from the high level inlet comprised mainly municipal wastewater with a hospital discharge equivalent to 1% of the flow. Sewage from the lower level inlet again comprised mainly municipal wastewater with an unspecified amount of trade effluent thought to be approximately 5-10%.

The activated sludge pilot plant 8 p.e. (Figure 5.1) was fed from the high level inlet and was designed to work under constant hydraulic loading (1 dry weather flow – DWF). The plant consisted of a 2.85 m^3 working volume primary sedimentation tank (PST) which fed both parallel activated sludge streams. The working volume of each of the two parallel completely mixed activated sludge (AS) tanks was 1.85 m^3 and each AS tank had a 0.5 m^3 working volume final settlement tank (FST) for secondary clarification. The dissolved oxygen (DO) concentration was maintained at 6-9 mg l^{-1} in both AS tanks to ensure effective mixing. To simulate the impact of return liquors one activated sludge stream operated with return liquors and the other without. The return liquors were an admixture of primary (60%) and humus (40%) sludges derived from the works treating the low level input sewerage and varying in age between 1-8 days storage at ambient temperature without mixing. The liquors were dosed directly into one of the aeration treatment tanks.

The pilot plant was initially seeded with mixed liquor from a full-scale ASP. Acclimation to the new settled sewage on site was allowed for by a four week period after which the experimental sampling programme commenced. By this time the effluent Biochemical Oxygen Demand (BOD) and suspended solids were consistently within the standard operating consent of 30 mg l^{-1} and 20 mg l^{-1}, respectively. Each set of operating conditions was maintained for a period of

two weeks after which the mixed liquor suspended solids (MLSS) concentration was adjusted downwards decreasing the SRT. The mean MLSS concentrations for the stream with return liquors were 4,870 mg l^{-1} (high MLSS; SRT=8 days), 3,438 mg l^{-1} (medium MLSS; SRT=4.3 days) and 2,383 mg l^{-1} (low MLSS; SRT=3.6 days). The mean MLSS concentrations for the stream without return liquors were 4,822 mg l^{-1} (high MLSS; SRT=8 days), 3,293 mg l^{-1} (medium MLSS; SRT=4.3 days) and 2,483 mg l^{-1} (low MLSS; SRT=3.6 days) (Table 5.3). The sampling points were as indicated in Figure 5.2.



(a)

(b)

(c)

Figure 5.1 Activated sludge pilot plant overview (a), primary sedimentation tank (b) and membrane separation unit (c)

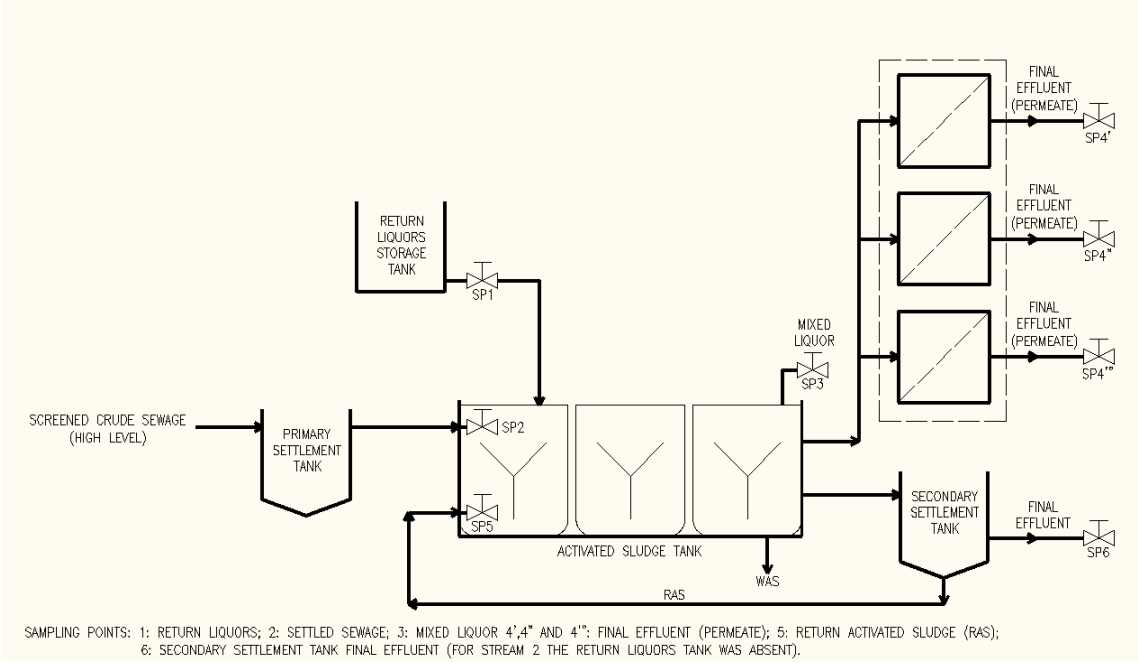


Figure 5.2 Schematic diagram of the activated sludge pilot plant, including both streams with and without return liquors, indicating the sampling point positions. The filtration units were operated on the stream with return liquors

Table 5.3 Activated Sludge pilot plant operating parameters

Average Operating Parameters/ MLSS	With Return Liquors			Without Return Liquors		
	High	Medium	Low	High	Medium	Low
Flow rate						
Settled Sewage, l h^{-1}	312	316	305	308	301	285
RAS, l h^{-1}	312	316	305	308	301	285
Return Liquors, l h^{-1}	6.0	8.4	9.2	0.0	0.0	0.0
WAS, l h^{-1}	1.0	5.5	8.6	0.0	4.4	9.0
Activated Sludge						
MLSS, mg l^{-1}	4870	3438	2383	4822	3293	2483
HRT, h	6	6	6	6	6	6
SRT, days	8	4.3	3.6	8	4.3	3.6
DO, mg l^{-1}	6.0	8.7	7.7	7.4	9.2	8.6
Temperature, ºC	16.6	13.4	13.2	17.0	14.3	13.8
pH	7.2	7.2	7.0	7.0	7.4	7.1
Settled sewage						
BOD, mg l^{-1}	116	99	157	116	84	150
sBOD, mg l^{-1}	56	37	66	55	30	66
COD, mg l^{-1}	299	249	388	308	237	374
sCOD, mg l^{-1}	133	116	211	127	81	216
N-NH_3, mg l^{-1}	24	20	28	24	20	26
Return liquors						
Suspended solids, mg l^{-1}	929.3	1120.4	441.0	n/a	n/a	n/a
Final effluent						
Suspended solids, mg l^{-1}	21.7	19.7	46.1	29.3	20.5	32.7
COD, mg l^{-1}	94.6	56.1	83.6	101	47.3	66.3
BOD, mg l^{-1}	10.5	8.6	15	13.8	6.5	11.9
NH_3, mg l^{-1}	0.4	0.4	0.5	0.4	0.4	2.4

n/a: not applicable

For enhanced filtration operation, mixed liquor from the activated sludge stream operating with return liquors was pumped to three parallel vertical multi-tube polysulphone membrane (Milleniumpore Ltd, Sunderland, UK) modules (with pore sizes 0.01, 0.08 or 0.4 μm) in place of the FST (Figure 5.1). Each module was 1.4 m in length and contained 50 mm and 60 mm diameter tubes providing a surface area of approximately 1.4 m^2. A submersible centrifugal pump (ITT Flygt, Nottingham, UK) was used to supply the membranes at a mean cross-flow velocity of 0.12 m s^{-1}. Supplementary air lift was used to provide coarse bubble aeration at a rate of 0.9 $Nm^3 h^{-1}m^{-2}$ of membrane area. The membrane system was flushed through with mixed liquor from the return liquor stream for at least 1 hour with a peristaltic pump (Watson Marlow, Falmouth, UK) prior to sampling. The operating average MLSS concentration was 3,626 mg l^{-1} during the period when the filtration system was applied.

5.2.2 Metal analysis

The glass and plastic ware used for collection, storage and manipulation of samples was soaked for a minimum of 1 hour in a 3% v/v Decon 90 (Fisher Scientific, Loughborough, UK) detergent solution prepared in ultrapure water (18.2 MΩ water PURELAB Ultra water purification system, ELGA, High Wycombe, UK) and then rinsed with the same source of ultrapure water. Subsequently they were soaked for a minimum period of 1 hour in a 1% v/v Primar Plus trace analysis grade nitric acid (Fisher Scientific, Loughborough, UK) prepared again in ultrapure water and following a final rinse in ultrapure water they were air dried.

Total metal analysis was undertaken on 30 ml samples placed in digestion tubes and acidified with 1.5 ml Optima ultra pure grade nitric acid (Seastar Chemicals Inc., Pittsburg, PA, USA). The samples were then digested in a MARSXpress microwave digester (CEM Microwave Technology, Buckingham, UK) to pre-set sample dissolution EPA method 3015 (US EPA, 2007). Every set of digested samples included a sample of Certified Reference Material (CRM) –

BCR-144R Sewage sludge of domestic origin (Laboratory of the Government Chemist, LGC, Teddington, UK). The samples were then transferred to 250 ml centrifuge tubes for analysis. Following digestion, the Cu samples were analysed using atomic absorption spectrophotometry (AAnalyst 800, Perkin Elmer Ltd., Beaconsfield, UK) equipped with a Zeeman-corrected transversely-heated graphite atomiser (THGA) and an AS-800 auto sampler. The Zn samples were analysed using the same AAnalyst 800 spectrophotometer using a burner system and an AS-90 auto sampler. The analytical conditions were those recommended by Perkin Elmer, utilising a multi-element hollow cathode lamp for both Cu and Zn and in all other respects analytical procedures conformed to those previously described (Sterritt and Lester, 1980a).

Samples for total metal analysis should contain a maximum of 100 mg of solids, if the sample contained more than 100 mg of solids; dilution with acidified ultrapure water was used to reduce the solids content to $\leq$100 mg. Batches of duplicate blanks, unspiked samples and samples spiked at low and high standard additions were analysed to determine accuracy variability and to characterise the method performance. Both total and dissolved samples, spiked at low and high additions exhibited no significant differences within or between batches with an overall recovery of 100% for both metals. To confirm the accuracy of the digested total metal samples, the Cu and Zn concentrations of the digested CRM sample were compared with its certified value and sample results and no adjustment was required for incomplete digestion as determined by the CRM value.

For dissolved metal analysis each sample was vacuum filtered through a Millipore all glass three piece vacuum filtering set (Millipore, Cambridge, UK) using a 0.45 µm pore size cellulose nitrate membrane filter (Anachem Ltd., Bedfordshire, UK). An aliquot of 30 ml (±0.1 ml) of the sample filtrate was then placed in a 50 ml centrifuge tube and acidified with 0.75 ml (±0.1 ml) of 2.5% volume Optima grade ultra pure nitric acid. Following acidification the samples were analysed by atomic absorption spectrophotometery as *per* total metals.

5.2.3 Suspended solids analysis

Total suspended solids analysis was determined within four hours of sample collection according to Standard Method 2540D (APHA, 1998) using grade GF/D glass microfibre filter papers (Whatman, Maidstone, UK).

5.2.4 Chemical oxygen demand

Determination of COD was carried out using a Merck Spectroquant (Nova 60 Spectrophotometer VWR International Ltd, Dorset, UK) COD cell test with the range of 500-10,000 mg COD l^{-1} (VWR, International Ltd, Dorset, UK). For soluble COD the samples were centrifuged at 12,000 *g* in a Rotanta 96 R centrifuge (Hettich Zentrigugen, Tuttlingen, Germany) for 20 minutes. The centrate was then decanted and filtered through a 0.45 µm pore size glass microfibre filter paper (Whatman, Maidstone, UK) prior to analysis.

5.2.5 Ammonium analysis

The analysis of ammonium (NH_4^+) was carried out using Merck Spectroquant Ammonium cell test having a range of 0.01-80 mg l^{-1} NH_4-N (VWR, Leicestershire, UK) using the method analogous to Standard Method 4500-NH_3D (APHA, 1998).

5.2.6 Temperature

The wastewater temperature was measured using a mercury in-glass-thermometer -10°C to +110°C (VWR International Ltd, Dorset UK).

5.2.7 Dissolved oxygen

The dissolved oxygen (DO) was determined using the Hach HQ20 meter equipped with a Luminescent Dissolved Oxygen (LDO®) probe (Hach Lange Ltd, Manchester, UK).

5.2.8 Total BOD analysis

The BOD was determined based on Methods for the Examination of Water and Associated Materials (1988) (Standing Committee of Analysts, 1988). The added seed was 5 ml final effluent per 500 ml of dilution water. Diluted samples were transferred to glass BOD bottles (Fisher Scientific, Loughborough, UK) and the dissolved oxygen determined using a Hach LDO meter (Camlab, Cambridge, UK).

5.2.9 Statistical analysis of data

The raw data was analysed using Minitab box plots to eliminate problems associated with outliers resulting from plant malfunction and abnormal flow conditions to the works *e.g*. storm events, to produce a data set amenable to further data analysis. Metal concentration factor calculations were completed according to Sterritt *et al.* (1981).

5.3 Results

5.3.1 The impact of mixed liquor suspended solids concentration (sludge age) on the removal of copper and zinc during activated sludge treatment

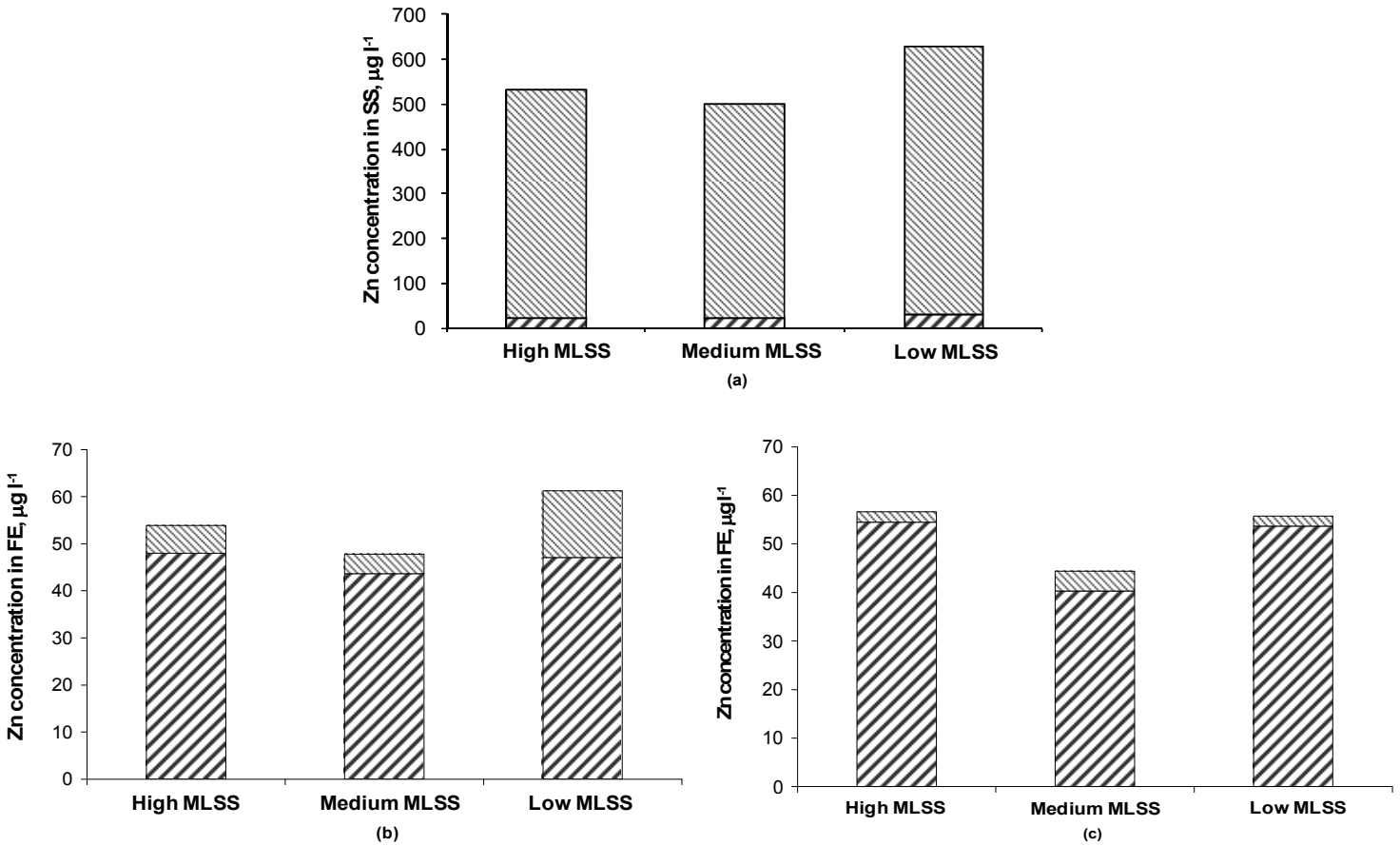
Sludge age or SRT is an important operating parameter for the activated sludge process and has a significant impact on final effluent quality in terms of suspended solids, BOD and nitrification. In order to evaluate the impact of this parameter on metal removal the pilot plant was operated with three different SRTs with return liquors added: 8 days (MLSS=4,870 mg l^{-1}); 4.3 days (MLSS=3,438 mg l^{-1}); and 3.6 days (MLSS=2,383 mg l^{-1}); and without return liquors 8 days (MLSS=4,822 mg l^{-1}); 4.3 days (MLSS=3,293 mg l^{-1}); and 3.6 days (MLSS=2,483 mg l^{-1}). At all three SRTs the pilot plant achieved a fully nitrified effluent with ammonia values typically 0.5 mg NH_3-N l^{-1}, whilst this is unusual at such low SRT this can be attributed to the constant hydraulic load, high DO values (6.5 mg l^{-1}) and relatively high temperatures (13-17ºC) throughout the study period. Similarly effluent BOD concentrations and suspended solids removal were also very good, typically >90% (Table 5.3).

Soluble and total concentrations of copper and zinc were determined twice daily and these values were averaged over the two week sampling period for each sludge age and were used to calculate the percentage removal (Table 5.4). Substantial removals of both total copper and zinc were achieved (*c.* >70 %). This was to be expected given the very low values for both effluent suspended solids (46-20 mg l^{-1}), BOD (7-15 mg l^{-1}) and COD (47-101 mg l^{-1}) (Table 5.3) and this can be partially explained by the operation of the pilot plant at constant hydraulic loading. However, for both metals the soluble fraction increased across the pilot plant indicating re-solubilisation. Solubilisation was greater for zinc than for copper (Figure 5.3; Figure 5.4). Similar values were obtained at all three SRTs and this probably reflects the similarity in residual effluent BOD/COD which was most probably the factor resulting in the solubilisation of these two elements.

Table 5.4 Percentage copper and zinc removal in the activated sludge pilot plant with and without return liquors

	SS conc., µg l^{-1}		FE conc., µg l^{-1}		% Removal	
	Soluble	Total	Soluble	Total	Soluble	Total
Cu – With Return Liquors						
High MLSS	1.6	17.0	2.3	4.5	-43.8	73.3
Medium MLSS	1.8	15.3	3.0	4.3	-66.7	72.1
Low MLSS	1.5	19.4	2.5	4.8	-66.7	75.3
Cu – Without Return Liquors						
High	1.6	17.3	3.4	5.2	-112.5	69.8
Medium	2.1	14.2	2.2	5.4	-4.8	61.8
Low	1.2	19.0	2.2	7.1	-45.5	62.8
Zn – With Return Liquors						
High	19.6	534	48.0	39.9	-145.0	92.5
Medium	19.1	500	43.7	47.8	-129.2	90.4
Low	26.0	631	47.1	62.0	-81.5	90.2
Zn – Without Return Liquors						
High	20.1	546	54.5	56.6	-170.3	89.6
Medium	19.5	478	40.3	44.4	-106.8	90.7
Low	26.6	632	53.6	55.7	-101.9	91.2

SS: Settled sewage; FE: Final effluent


Zn concentration in SS, µg l-1
700
600
500
400
300
200
100
0
High MLSS
Medium MLSS
Low MLSS
(a)
Zn concentration in FE, µg l-1
70
60
50
40
30
20
10
0
High MLSS
Medium MLSS
Low MLSS
(b)
Zn concentration in FE, µgl-1
70
60
50
40
30
20
10
0
High MLSS
Medium MLSS
Low MLSS
(c)

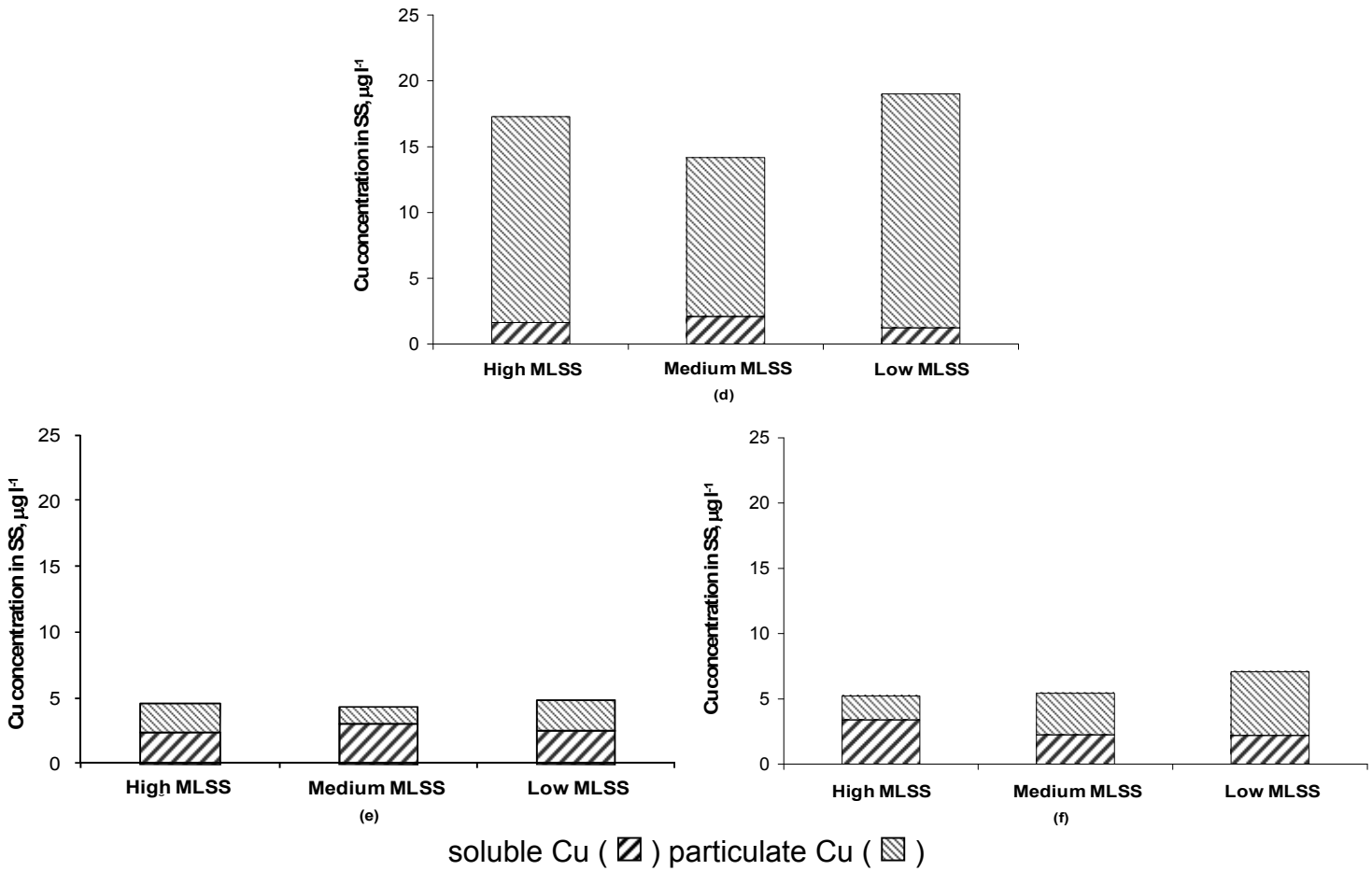
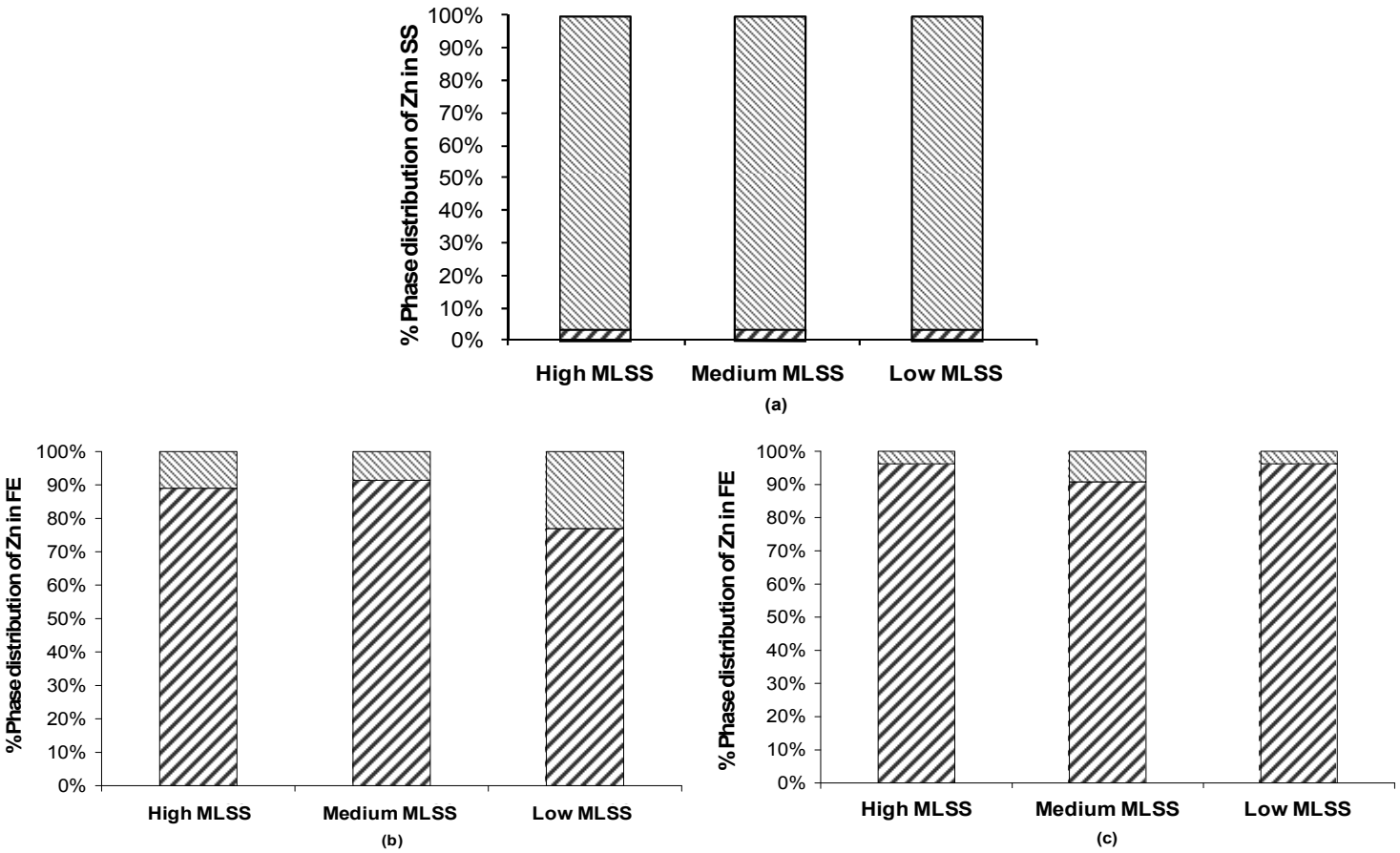


Figure 5.3 Phase distribution concentration of zinc and copper in settled sewage (SS) (a) for Zn (d) for Cu and in final effluent (FE) for the stream with return liquors (b) for Zn and (e) for Cu and for the stream without return liquors (c) for Zn and (f) for Cu


% Phase distribution of Zn in SS
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
High MLSS
Medium MLSS
Low MLSS
(a)
% Phase distribution of Zn in FE
High MLSS
Medium MLSS
Low MLSS
(b)
% Phase distribution of Zn in FE
High MLSS
Medium MLSS
Low MLSS
(c)

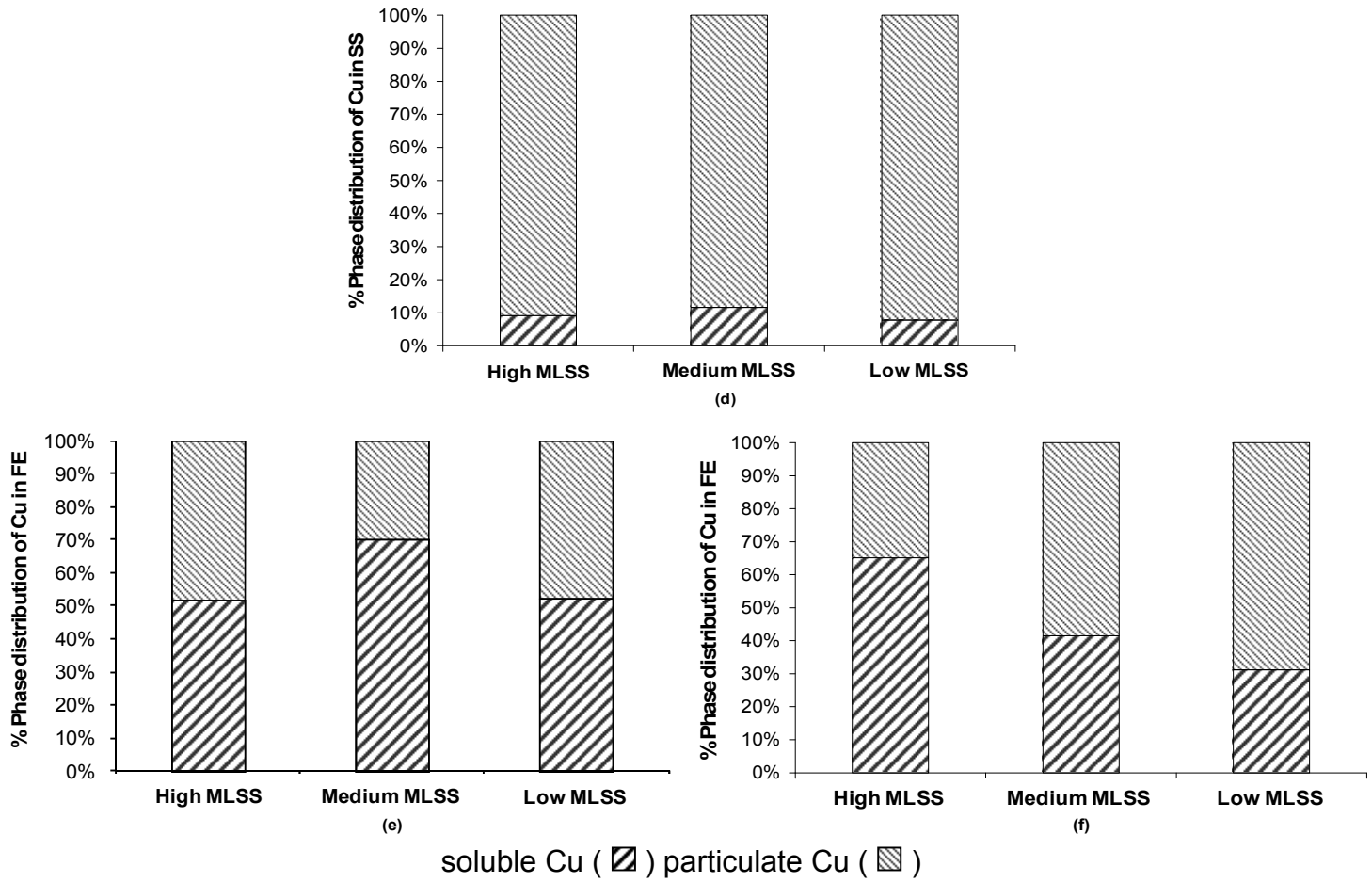


Figure 5.4 Phase distribution percentage of zinc or copper in settled sewage (SS) (a) for Zn (d) for Cu and in final effluent (FE) for the stream with return liquors (b) for Zn (e) for Cu and for the stream without return liquors (c) for Zn and (f) for Cu

The accumulation of heavy metals in the mixed liquor at the different sludge ages was expressed as a function of the mixed liquor suspended solids and the total quantity of metal entering the system during the sampling period. This concentration factor (CF) was given by equation (5.1) (Sterritt and Lester, 1981):

$$CF = \frac{ML_C * ML_V}{MLSS * ML_V * I_C * I_V} \quad \textbf{(5.1)}$$

Where:

ML_C = mean concentration of metal in mixed liquor (mg l^{-1})

I_C = mean concentration of metal in influent (mg l^{-1})

ML_V = volume of mixed liquor (l)

I_V = volume of influent entering over a 5 days sampling period (l)

$MLSS$ = mixed liquor suspended solids concentration (mg l^{-1})

Both the medium and high sludge ages had a higher sludge adsorption capacity for both copper and zinc in comparison to the low sludge age (Figure 5.5). There was however, a reduction in adsorption capacity at the high sludge age (1.77E10^{-8} mg^{-1}) from 2.07 E10^{-8} mg^{-1} at the medium sludge age for zinc which is probably due to the metal solubilisation reported above.

The CF for copper and zinc was observed to be consistently lower with the addition of liquors (Figure 5.5). This is not unexpected as the available surface area has been increased by the addition of liquor suspended solids, which were low in adsorbed metal. Therefore, based on an adsorption *per* mg of solids the adsorption capacity would be reduced.

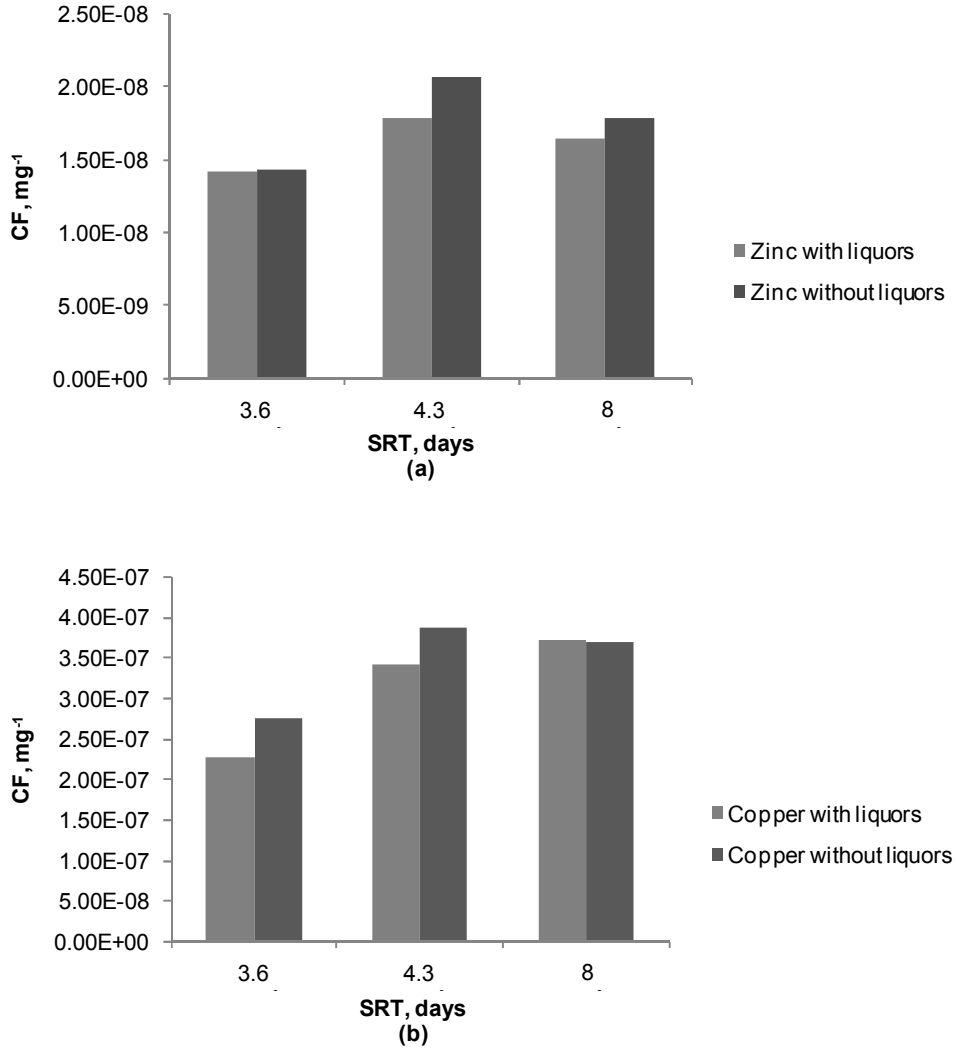


Figure 5.5 The accumulation of zinc (a) and copper (b) in the activated sludge mixed liquors at three different sludge ages (low, medium and high) both with and without liquors expressed as a concentration factor (CF).

5.3.2 The impact of effluent suspended solids and BOD/COD on metal removal

Increases in SRT are normally associated with improvements in effluent quality particularly with respect to effluent suspended solids and residual organic matter (COD/BOD). From examination of Table 5.3 it is evident that at all three SRTs studied there was less variation in effluent suspended solids between the high and the medium SRT (Table 5.3). However, higher suspended solids were observed at the low SRT typically 32.7-46.1 mg l^{-1}) without and with liquor addition respectively. The COD (with and without liquors) was typically 47.3-101 mg l^{-1} and the BOD (with and without liquors) 6.5-15 mg l^{-1}. However, overall there were no substantial differences in total metal removal with 61.8-75.3% and 89.6-92.5% total copper and zinc removal respectively observed (Table 5.4). Nevertheless, as described above the proportion of soluble metal increased across both the activated sludge processes. The extent of this was always greater for zinc in comparison to copper (Figure 5.3; Figure 5.4) and the highest SRT gave the highest re-solubilisation for zinc.

This would support the hypothesis that at higher SRT organic ligands are produced which enhances metal solubility. In the case of copper no clear solubilisation trend was apparent over the three sludge ages.

5.3.3 The role of return liquors on metal removal

It is possible that return liquors could affect metal removal in one of two ways, firstly because they are high in heavy metals they could contribute to the final effluent concentration, thus causing deterioration in final effluent quality. Alternatively, since they are also high in suspended solids they could provide additional surface area that may enhance metal adsorption and subsequently, upon settlement by removal with effluent suspended solids, enhance metal removal with the consequent improvement in effluent quality. To test this hypothesis, samples of settled sewage and final effluent with and without return

liquors were filtered through a 0.45 µm membrane to separate the soluble phase from the particulate for both zinc and copper (as described in methods). The effect on the concentrations of copper can be seen in Figure 5.3. It is readily apparent that there is a very substantial reduction (*c.* 70 %) between settled sewage and final effluent particulate copper concentrations. It is not easy to determine a difference between the effluents with and without liquors, to facilitate this comparison the data are presented as percentages in Table 5.4. It would appear that there is a small (15%) but consistent reduction in soluble metal concentration in the presence of return liquors (Table 5.3).

Examining Figure 5.3 it appears quite clear that concentrations of soluble zinc are greater in the absence of return liquors. When this is examined as a percentage (Figure 5.4) it is apparent that overall there is 20% less soluble zinc in the presence of return liquors. This would suggest that return liquors may play a role in enhancing metal removal rather than increasing the metal concentrations in the effluent.

5.3.4 Identification of the predominant characteristics controlling final effluent metal concentration

The final effluent metal concentrations were examined using rank percentile plots (Figure 5.6; Figure 5.7) to determine if there was one parameter which was paramount in controlling overall metal removal and thus final effluent concentration. The factors taken into account in this analysis included SRT and the absence or presence of return liquors. Examining Figure 5.6 for zinc it is apparent that the graphs are clearly divided into two groups. The low SRT (3.6 days; low MLSS) for zinc with and without liquors is in a separate population from the other treatments with higher effluent zinc concentrations. For example, at the 50 percentile point a higher total zinc effluent concentration of 57.5-64.4 µg l^{-1} was observed for the low SRT (3.6 days) compared with 35-38.2 µg l^{-1} from the 4.3 and 8 day SRT treatments. Therefore, although small differences in total zinc removal 89.6-92.5% were observed these were not significant,

nonetheless a detrimental effect on total metal removal at the low SRT was clearly evident for zinc with final effluent 50 percentile concentrations of 57.5-64.4 µg l^{-1} observed at the low SRT in comparison to 35-38.2 µg l^{-1} at the higher SRTs.

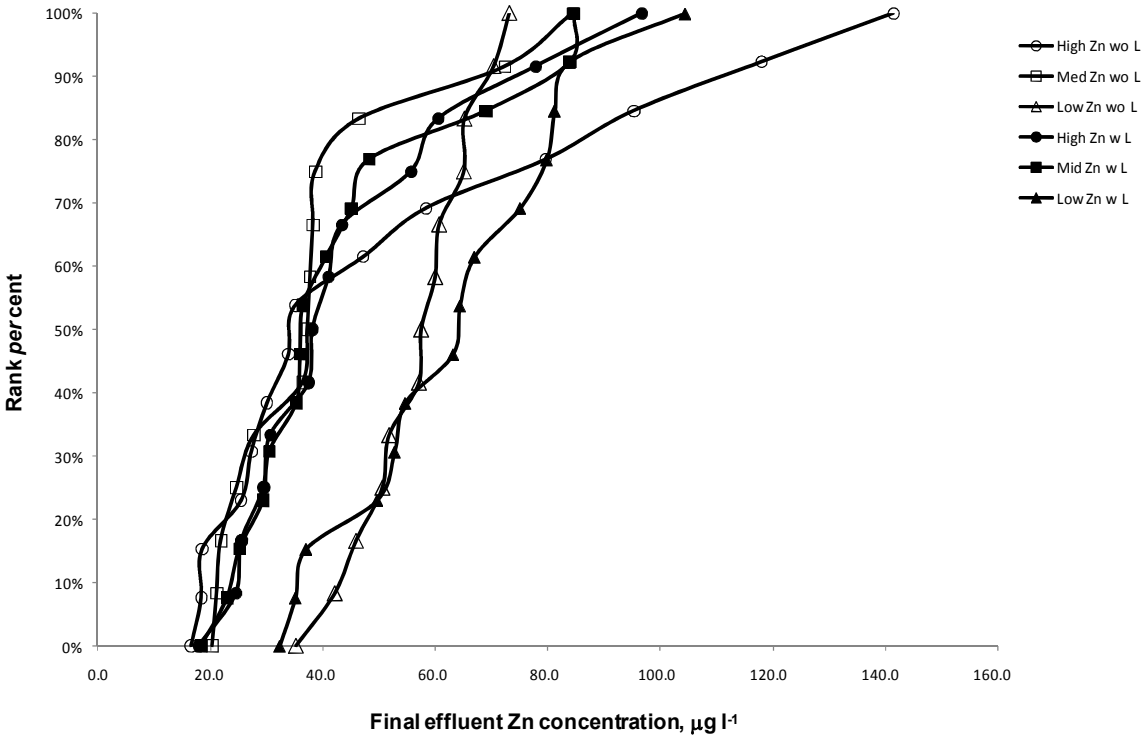


Figure 5.6 Percent ranked final effluent total zinc concentrations with (w L) and without return liquor (wo L) additions at the three different mixed liquor concentrations

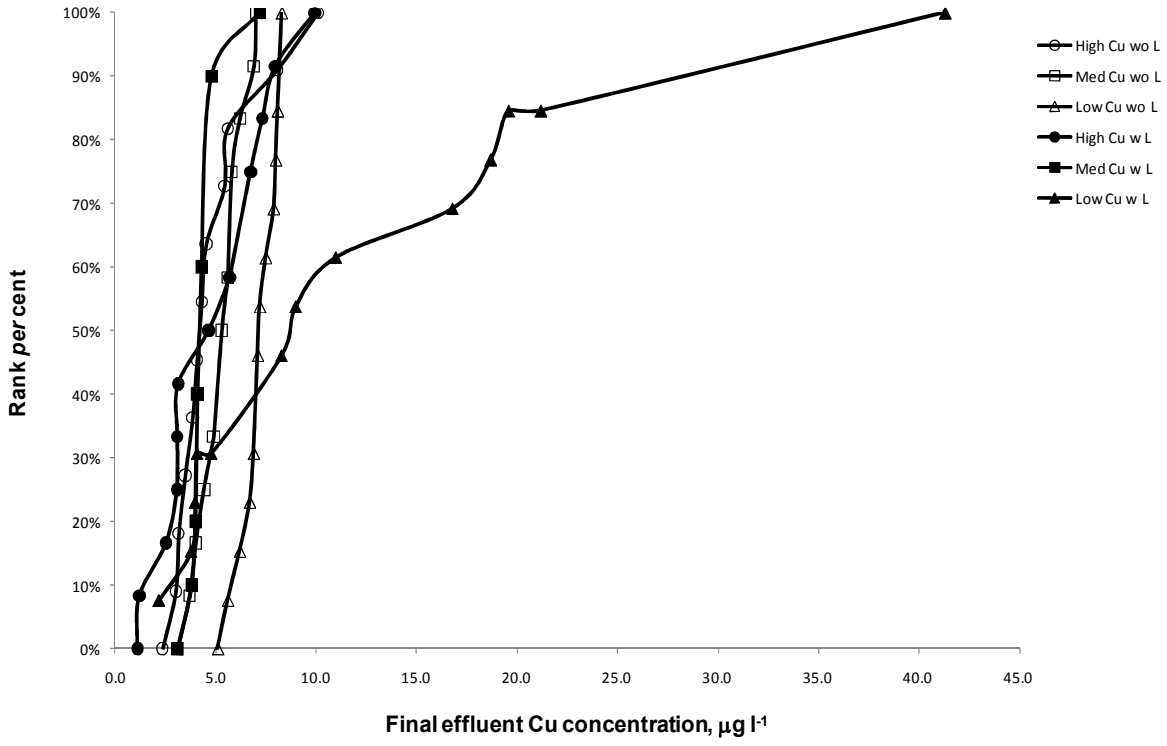


Figure 5.7 Percent ranked final effluent total copper concentrations with (w L) and without return liquor (wo L) additions at the three different mixed liquor concentrations

Return liquors appeared to result in an increased overall range of total zinc concentrations observed in the final effluent from 32.4-104.4 µg l^{-1} with liquors to 35.2-73.2 µg l^{-1} without liquors addition at the low SRT. However, at the high SRT this was reversed with the larger range in total zinc final effluent concentrations observed without liquor addition (16.6-141.4 µg l^{-1}) compared to with liquor addition (18-96.7 µg l^{-1}). Since the role of the added return liquors would appear to enhance metal adsorption, it is speculated that this effect will be more pronounced at the high SRT due to the higher re-solubilisation of zinc which was observed at this SRT.

The low SRT populations for total copper were similar to the zinc data with higher 50 percentile point effluent concentrations at 7.2-9 µg l^{-1} in comparison to 4.1-5.3 µg l^{-1} for the medium and high SRT conditions (Figure 5.7). Although the

separation of the populations was less pronounced than for zinc (Figure 5.6) a potential detrimental effect on total copper effluent concentrations was still observed in the low SRT treatment process.

The impact of return liquors on the range of copper effluent concentrations observed was less pronounced than for zinc. The range in final effluent total copper concentrations at the high SRT with liquors was 1.1-9.9 µg l^{-1} which was approximately equivalent to the effluent concentration range without liquors at 2.4-10.1 µg l^{-1} indicating limited lowering of effluent copper concentrations with the addition of return liquors.

Overall, examination of the rank percentile data suggests that the SRT is of paramount importance in determining metal removal. The impact of return liquor addition was beneficial in terms of reducing metal effluent concentrations at the high SRT (8 days) when more of the metal was available for adsorption by the additional suspended solids added with the return liquors.

5.3.5 Possible role of membranes as a tool to enhance metal removal

Membrane bioreactors operating at high SRTs are generally accepted to produce high quality effluents in respect to effluent BOD and in particular suspended solids (values <1.0 mg l^{-1}). Whilst this study was not undertaken with a MBR, and therefore impacts on effluent BOD could not be determined, the incorporation of a membrane phase separator to examine the effect on suspended solids and metal removal from the mixed liquor developed in the activated sludge pilot plant was evaluated. The trial membrane separation unit included membranes with three pore sizes (0.01, 0.08, 0.4 µm) for comparative purposes.

The membrane was applied to the stream containing return liquors whilst operating at a SRT of approximately 8 days. Effluent suspended solids were non-detectable for all three membranes. Residual BOD and COD were 8.5 and

67 mg l^{-1} respectively. The results for metal removal are presented in Table 5.4 and by comparison with Table 5.5 it is apparent that there is an overall improvement in the percentage removal for copper which averaged approximately 73% with the secondary clarifier and 99.5% with the membrane. For zinc the removal percentage for the secondary clarifier was approximately 91% and that for the membrane averaged 98%. Therefore, the membrane results in a performance improvement of *c.* 25% for copper and *c.* 8% for zinc. No clear change in the percent removal for both copper and zinc was observed between the different membrane sizes (0.01, 0.08, 0.4 µm).

This improvement in metal removal by using membranes for phase separation is unlikely to be observed under real conditions with an actual MBR due to the effect of high sludge ages on the bacterial production of ligands which will cause enhanced metal solubility and deleteriously impact on metal removal.

Table 5.5 Copper and zinc removal rates of an activated sludge pilot plant with membrane filtration

		SS		MLSS*		FE			% Removal		
						Pore size, µm			Pore size, µm		
		Sol.	Total	Sol.	Total	0.01	0.08	0.40	0.01	0.08	0.4
Cu	Mean, µg l^{-1}	0.9	34	2.3	762.9	3.0	2.7	4.4	99.6	99.6	99.4
	SD	0.5	3.8	1.2	80.1	1.2	0.2	1.3	n/a	n/a	n/a
Zn	Mean, µg l^{-1}	33.6	554.6	26.7	2205.7	13.0	13.5	14.0	99.4	94.4	99.4
	SD	4.7	11.8	4.9	216	1.8	2.5	2.3	n/a	n/a	n/a

*Average MLSS: 3,626 mg l^{-1}; n/a: not applicable; Sol.: Soluble;
% removed calculated from ((Total MLSS–FE)/Total MLSS)*100

5.4 Discussion

The potential mechanisms of metal removal during biological wastewater treatment have been outlined (Ziolko *et al.*, 2010; Brown and Lester, 1979; Crane *et al.*, 2010). Volatilisation has never been observed in full-scale works or pilot plants for those elements to which it is potentially applicable, *i.e.* those that can be biologically converted to volatile organo-metallics, or in the case of mercury biologically reduced to the volatile elemental form. On the contrary when studied at full-scale arsenic and mercury were fully accounted for by mass balances and did not indicate any significant losses to atmosphere (Goldstone *et al.*, 1990a). Although active uptake of metals into the cell may be observed in pure cultures (Webb, 1970; Tynecka *et al.*, 1981; Norris and Kelly, 1977), evidence for this in a lab-scale activated sludge biomass was only found for nickel with evidence of perhaps very limited uptake (approximately 8%) for copper (Lawson *et al.*, 1984c). For the other metals studied cadmium, cobalt, manganese, nickel and thallium no positive effect was found and this may reflect the low viability of activated sludge bacteria due to their very low growth rate (Lawson *et al.*, 1984c). Based on this evidence it is reasonable to conclude that the major pathways for metal removal in the activated sludge process (and its derivatives) are entrapment of insoluble particulate metal within the settleable floc matrix and binding to extracellular polymeric materials. Opposing these mechanisms are those factors, which prevent precipitation by maintaining metal solubility (Stoveland and Lester, 1980).

Solubility of metals maybe enhanced by ligands present in the influent settled sewage or generated by the activated sludge bacteria. These ligands can be natural, inorganic or organic molecules (Stumm and Morgan, 1970) or anthropogenic compounds (Cheng *et al.*, 1975; Neufeld and Hermann, 1975); particularly effective examples are synthetic organic molecules such as *EDTA* (Perry *et al.*, 1984) and *NTA* (Stoveland *et al.*, 1979). For metals which are present as ligands to be removed by biological wastewater treatment they must undergo either chemical or biological breakdown. Some inorganic molecules which are able to chelate metals, *e.g*. sodium tripolyphosphate and sodium

hexametaphosphate undergo hydrolysis in complex matrices such as wastewater breakdown to phosphates and as a consequence releasing the metal into solution (Perry *et al.*, 1984). However, the predominant chelating species present appear to be organic in nature and the principal mechanism of their breakdown is aerobic biodegradation. The sources of organic ligands in mixed liquor are:

- settled sewage (influent sources)
- secreted bacterial products, principally extracellular polysaccharides
- bacterial products of lysis *e.g.* nucleic acids, proteins, carbohydrates.

Whilst pure cultures of bacteria growing at relative high growth rates (doubling times measured in hours) secrete pure extracellular polysaccharides to produce capsules (Wilkinson, 1958; Sutherland, 1972), in activated sludge with extremely low growth rates (doubling times measured in days), cell viability is very low and cell lysis consequently common. As a result the extracellular polysaccharides (EPS) contains all the products of cell lysis and this material is commonly referred to as extracellular polymeric material (EPM) to denote its heterogeneous nature, as opposed to EPS which for any given bacterial species is a homogeneous polysaccharide (Wilkinson, 1958; Novak *et al.*, 1977). Both EPS and EPM have been extensively studied to determine their possible role in metal absorption by activated sludge biomass (Rudd *et al.*, 1984a; Brown and Lester, 1982a; Brown and Lester, 1982b; Rudd *et al.*, 1983b; Rudd *et al.*, 1984b; Uloth and Mavinic, 1977; Rudd *et al.*, 1983a; Bitton and Freihofer, 1977). However, the role of EPM is not always clear. It has been reported that the removal of the soluble form of some metals notable copper (Rudd *et al.*, 1984a; Stephenson *et al.*, 1987), cadmium and also nickel under some conditions (Rudd *et al.*, 1984a) involves EPM. It can however change its physical form and “slough-off” from the cell, it is assumed that in this form it still binds the metal but now retains it in solution (Rudd *et al.*, 1983b). In the endeavour to rationalize the fate, behaviour and removal of metals in activated sludge biomass (mixed liquor), SRT or sludge age (θc), effectively the average

bacterial growth rate (or doubling time) of the bacteria in the biomass has been recognized as an overarching factor and extensively studied (Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c; Stephenson and Lester, 1987a; Stephenson and Lester, 1987b; Stephenson *et al.*, 1987). Sludge retention time determines:

- mixed liquor suspended solids concentration;
- effluent suspended solids concentration;
- effluent BOD/COD;
- bacterial species composition and diversity and hence nature of surface area and EPS composition; and
- extent of lysis and hence EPM composition.

It has been proposed that the quantity of biomass is important in metal removal (Stoveland and Lester, 1980; Kempton *et al.*, 1983; Lawson *et al.*, 1984c) the greater the biomass the greater the removal. Conversely if metals are taken up by the biomass, but biomass escapes as effluent suspended solids this will reduce total removal (Stoveland and Lester, 1980; Sterritt *et al.*, 1981; Stephenson and Lester, 1987b). Effluent BOD and COD have been used as surrogate measures of organic ligands or chelants able to retain metals in solution and thus prevent removal (Sterritt *et al.*, 1981; Lawson *et al.*, 1984b; Stephenson and Lester, 1987a; Stephenson *et al.*, 1987). These are imprecise measures, since they measure organic molecules without chelating capacity as well as those with. Nevertheless effluent BOD and COD have proved of value in the absence of a more precise parameter. Although numerous attempts to determine the actual complexing compounds have not yielded any definitive information, their complexation capacity suggests they are only a small proportion of the total BOD/COD (Lawson *et al.*, 1984a; Rudd *et al.*, 1984a; Rudd *et al.*, 1983b; Rudd *et al.*, 1984b). The variety of these complexing compounds in settled sewage and those synthesized biologically in activated sludge has been demonstrated by the application of gel permeation

chromatography (Sterritt and Lester, 1982; Rossin *et al.*, 1982; Kempton *et al.*, 1983; Lawson *et al.*, 1984d).

The SRT will also influence numbers of bacterial species present (diversity) and this is known to increase at higher SRT values (Metcalf & Eddy *et al.,* 2003). Notable amongst these changes will be the survival of autotrophic nitrifying bacteria (Metcalf & Eddy *et al.,* 2003). With these changes (increase) in bacterial diversity there will be associated changes in the chemical composition of the bacterial cell surface and the EPS secreted. Similar there would be changes in the bacterial products/metabolites released into solution. In addition with increasing SRT *i.e*. lower growth rate, lysis would increase and more nucleic acid, proteins and carbohydrates would be available for incorporation into the EPM (Lawson *et al.*, 1984c; Rudd *et al.*, 1983a; Wilkinson, 1958). Moreover, the nature of the polysaccharides in the EPS would be influenced by the changes in the bacterial population.

The complexation capacity and stability constants of MLSS and EPM are very similar, which strongly supports the hypothesis that they are the same thing, these properties of MLSS are conferred upon them by their EPM (Rudd *et al.*, 1984a; Rudd *et al.*, 1983b; Rudd *et al.*, 1984b). Complexation capacity would not directly appear to be significantly affected by SRT of the biomass (Rudd *et al.*, 1983b). However, an indirect and significant effect could occur if the EPM is “sloughed off” from the bacterial capsule into solution carrying with it the complexed metal and the metal previously attached to the settleable biomass would be transferred into the soluble non-settleable phase. Only small changes in cultural conditions (operating parameters) appear to be required to bring about this transposition (Rudd *et al.*, 1983b; Saunders and Dick, 1981). In cultures of *Kebsiella aerogenes*, an EPS producing organism whose EPS binds metals, at high growth rates 95% of the EPS was soluble and maintained metal in solution, as growth rate diminished, solubility of EPS was reduced until at the lowest growth rate studied only 7% of EPS was soluble and metal removal increased (Rudd *et al.*, 1983b). In a study of activated sludge the same trend was observed as sludge age increased and thus growth rate fell more of the

EPS/EPM became insoluble aiding metal removal at the highest sludge age studied when the solubility of the EPS/EPM was the lowest observed (Saunders and Dick, 1981). The changes in binding which occur with the transition of EPS and EPM from the soluble to insoluble state require elucidation if metal removal is to be optimized, there is evidence that the binding sites themselves may change in conjunction with this physical change in the nature of the EPS/EPM (Steiner *et al.*, 1976; Gould and Genetelli, 1978; Haug and Smidsrød, 1967).

The potential impact of SRT on metal removal in the activated sludge process can be seen in the studies of Stephenson *et al.* (1987a; 1987b). These studies are reproduced in Figure 5.8 and Figure 5.9 (Stephenson and Lester, 1987b) and are intended to not only characterize the effect of sludge age on metal removal, but also the importance of biomass in the removal of insoluble metal. In this study mixed liquors from a pilot-scale activated sludge plant treating settled sewage operating at 3, 6, 9 and 12 days sludge age were examined to determine their impact on the removal of metals in the presence and absence of biomass. Samples of biomass at each sludge age were filtered through 0.2 µm filters to remove all bacterial cells. Mixed liquors and mixed liquor filtrate were then spiked with metal solutions to achieve metal concentrations in the mixed liquor or its aqueous matrix consistent with concentrations reported in (Rossin *et al.*, 1982; Kempton *et al.*, 1983) and comparable to concentrations of heavy metals reported in municipal wastewaters (Stoveland *et al.*, 1979; Rossin *et al.*, 1982). From comparison of Figure 5.8 and Figure 5.9 it is evident that sludge age has no significant effect on soluble metal concentrations which are typically 5% or less for both copper and zinc. In the absence of biomass soluble metal concentrations are slightly greater up to 8%. Evidently the majority of both metals are insoluble in the absence of biomass, but very little is settleable in the absence of biomass. In the presence of biomass a clear trend becomes evident. At low SRT, 3 days, removal is low (60%), but at 6 days and above removal is much higher 85-95%. Presumably the consequence of the generation of a mixed liquor with superior settling characteristics (higher SSVI).

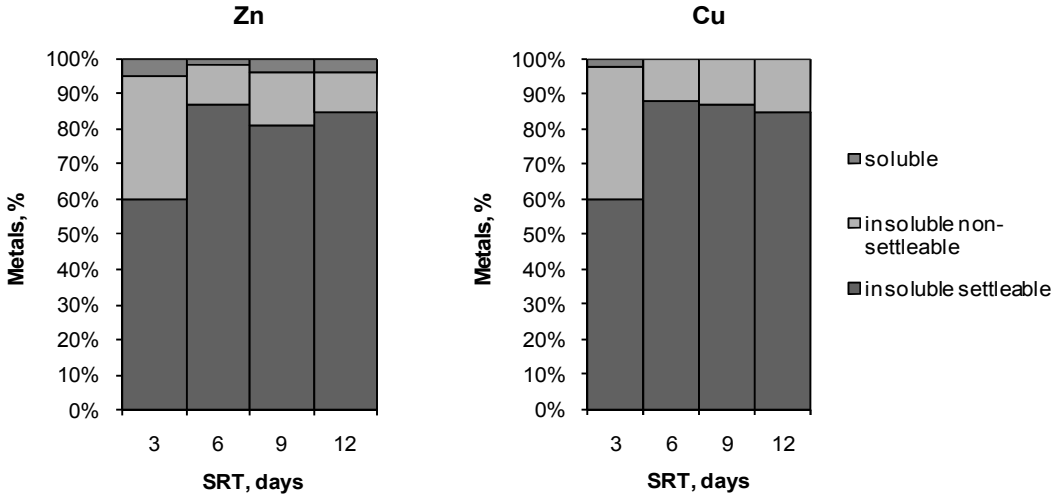


Figure 5.8 Percentages of insoluble settleable, insoluble non-settleable and soluble copper and zinc in the presence of mixed liquor solids at SRT of 3, 6, 9 and 12 days. Adapted from Stephenson *et al.,* (1987b).

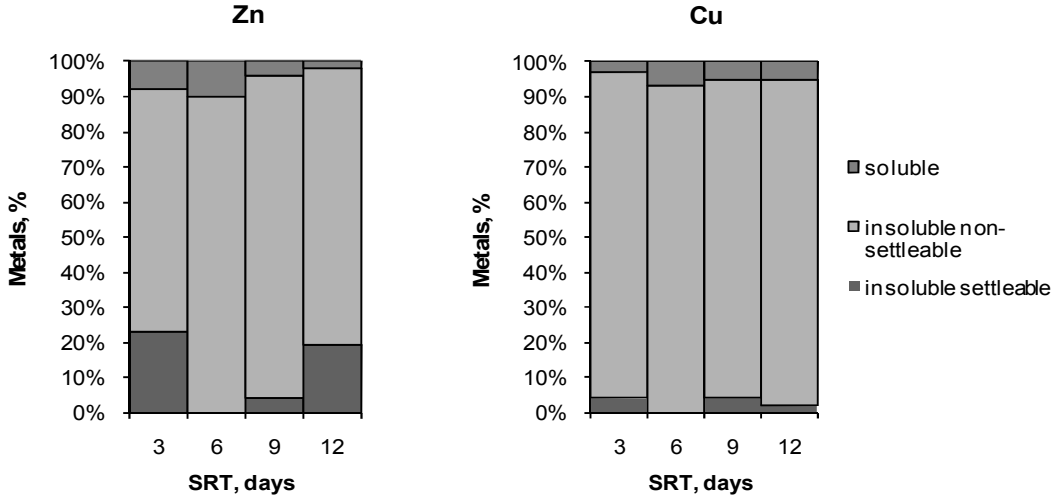


Figure 5.9 Percentages of insoluble settleable, insoluble non-settleable and soluble copper and zinc in the mixed liquor filtrate (no biomass) at SRT of 3, 6, 9 and 12 days. Adapted from Stephenson *et al.,* (1987b).

The impact of sludge age on metal removal has been extensively studied and it has been found that in general medium to high SRT (6-12 days) favour metal removal (Sterritt and Lester, 1981; Sterritt and Lester, 1982; Kempton *et al.*, 1983; Rudd *et al.*, 1984a; Stephenson *et al.*, 1987; Lester *et al.*, 1983). It has been postulated that at low sludge ages chelators present in the settled sewage are not fully biodegraded and retain metals in solution, whilst at high sludge age, products of bacterial metabolism and extracellular polymers “slough-off” from the cell retaining metals in solution. Both mechanisms are detrimental to metal removal (Rossin *et al.*, 1982; Kempton *et al.*, 1983; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c; Lawson *et al.*, 1984d; Stephenson and Lester, 1987a; Stephenson and Lester, 1987b). Thus, as sludge age increases, initially metal removal is enhanced as chelators present in the settled sewage are eliminated by biodegradation, thus rendering more of the metal insoluble and enhancing the proportion of metal amenable to removal by incorporation into the settleable biomass (Figure 5.10).

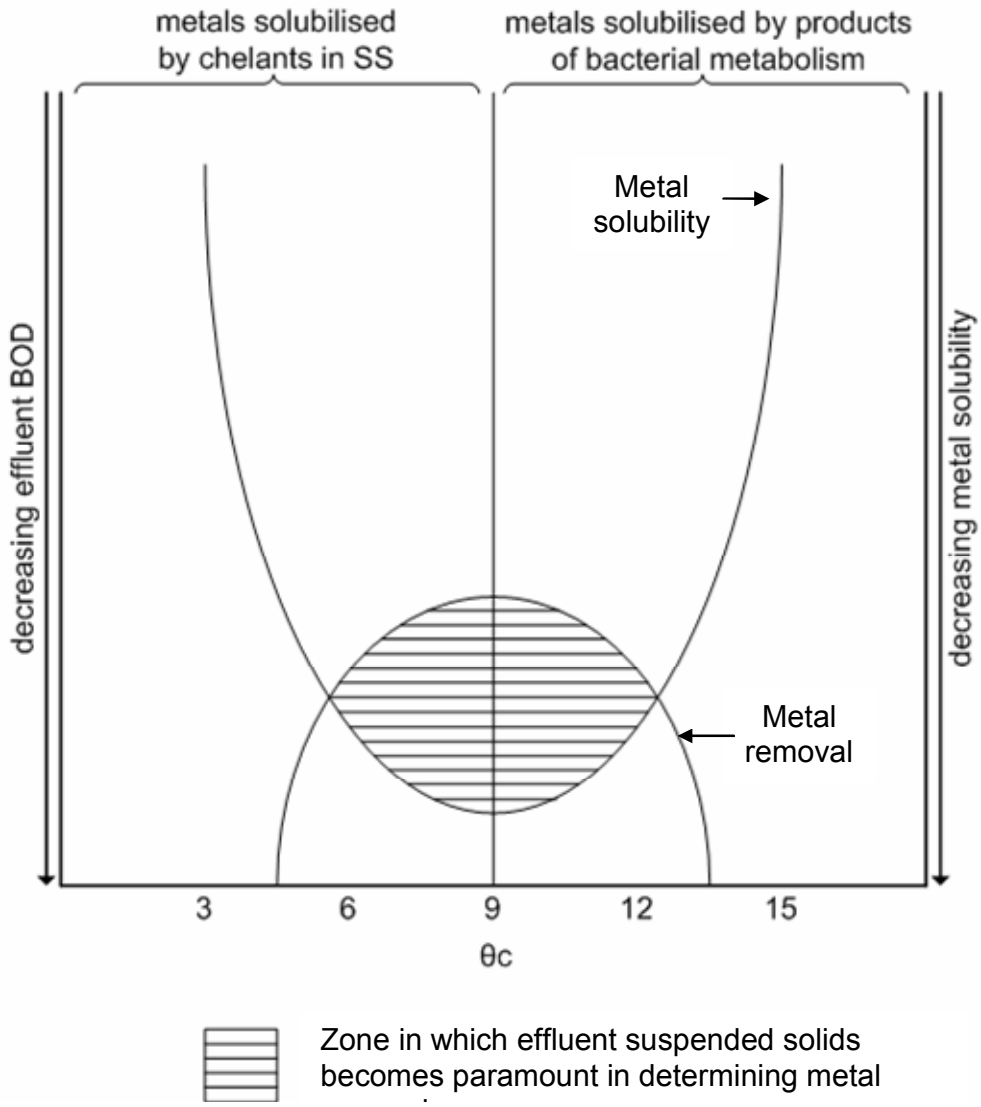


Figure 5.10 Schematic hypothetical representation between metal solubility, sludge age and the relative importance of effluent suspended solids

However, further increases in SRT, whilst maximising destruction of ligands present in the settled sewage, concomitantly result in the production of chelators by the mixed liquor biomass, rendering the metals soluble and unavailable for incorporation into the settleable biomass, thus reducing removal. Between these extremes is a point at which solubilisation is minimal and incorporation into the settleable biomass is maximised. At this point removal of

effluent suspended solids becomes paramount in determining metal removal. However, this situation only arises when the destruction of biodegradable chelators in the settled sewage has been maximised and before metal solubility is adversely affected by the production of natural metal chelators by the activated sludge mixed liquor. This optimum point varies according to site, process design, sewage composition *etc*., but in general appears to be in the range of sludge ages between 8-15 days.

5.5 Conclusions

- Removal of both copper and zinc was greater at SRT of 4.6 and 8 days when compared to removals observed at 3.6 days. It is postulated that this is directly related to higher removal of both BOD and suspended solids observed at these higher sludge ages.

- It is hypothesised that the biodegradation of ligands in the influent settled sewage at higher sludge ages rendered more of the copper and zinc insoluble, and thus amenable to co-settlement and this is of significance in the higher removals observed.

- The introduction of return sludge liquors, high in settleable solids immediately prior to aeration, moderately enhanced the removal of copper and zinc.

- The use of membranes in place of secondary sedimentation, maximizing effluent suspended solids removal (<1 mg l^{-1}) enhanced removal of both copper and zinc. However, no benefit in overall metal removal would be expected from the introduction of MBRs. Since the impact of improved suspended solids removal would be negated by the enhancement in metal solubility caused by the production of metal solubilising ligands at the high sludge ages at which MBRs normally operate.

- Overall entrapment of insoluble metal by settleable biomass is paramount in metal removal, this depends on maximising biodegradation of chelators present in the settled sewage minimising production of chelators by the biomass and subsequently maximising effluent suspended solids removal. For some metals, including copper, adsorption of soluble metal by EPM may play a secondary role in their removal.

5.6 References

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6 METALS SPECIATION

Ana Santos and Simon J. Judd

6.1 Introduction

Wastewater is an unpredictable dynamic matrix making definition of the physichochemical forms of the metals present extremely challenging (Chapter 2; Chapter 5; Appendix A). The increasing awareness of the impact of metals on the environment is mainly attributed to its toxicity (Chapter 2), and largely dependent on their speciation (Allen *et al.*, 1980) such that an understanding of speciation is essential in defining toxicity. Metal complexation with the extracellular polymers is known to reduce its toxicity (Bitton and Freihofer, 1977).

Metals are removed during conventional treatment and there are several factors influencing metals biosorption and its removal (Chapter 2; Chapter 5; Appendix A). The plant operation parameters influence the metal removal efficiency by shaping the physicochemical characteristics of the extracellular polymers (Chapter 2; Chapter 5; Appendix A). More than a biological process, metal biosorption is a physicochemical interaction between the metal and functional groups on the cell surface, based on physical adsorption (Brown and Lester, 1982a), ion exchange (Chang *et al.*, 1995), complexation (Brown and Lester, 1982a) and precipitation (Oliver and Cosgrove, 1975; Ledin, 2000).

6.2 Complexation of metals with organic matter

Factors known to play an important role in metal biosorption are those influencing the binding sites local environment or chemical nature (Artola and Rigola, 1992), and as such mainly comprise solution pH (Nelson *et al.*, 1981; Baudu *et al.*, 2000), metal type/species (Rossin *et al.*, 1982; Mehrotra *et al.*, 1991), ionic strength and temperature (Al-Qodah, 2006; Brown *et al.*, 1999),

bacteria cell surface properties (Sag and Kutsal, 1995), ligand composition, and general composition and characteristics of the solution or solids (Battistoni *et al.*, 1993). The biochemistry is complex due to the many species of bacteria co-exist on the activated sludge, such as the *Klebsiella, Bacillus, Pseudomonas, Azobacter* and *Zoogloea* (Lester, 1987). This wide variety is essential for an efficient contaminant removal as each species is normally able to break down only one type of carbon substrate present in the wastewater.

Extracellular polymeric substances (EPS) represent a key component of activated sludge, and are known to play an important role in metals removal resulting from active bacterial secretion, shedding of cell surface material, cell lysis materials (Brown and Lester, 1982a; Guibaud *et al.*, 2003; Liu *et al.*, 2001). Their chemical make-up is diverse, with carbohydrates and proteins being the major constituents but including humic substances, uronic acids and nucleic acids in smaller quantities (Liu and Fang, 2002; Sponza, 2002; Sponza, 2003; Wingender *et al.,* 1999; Liu and Fang, 2003). These organic materials containing inorganic functional groups such as carboxyl, phosphoric, amine, and hydroxyl groups (Liu and Fang, 2002), representing potential binding sites for metal ions (Brown and Lester, 1982a; Liu and Fang, 2002; Brown and Lester, 1982b).

Often, wastewater contains not only natural organic chelating ligands, including EPS and allochthonous materials such as fulvic and humic acids, but also anthropogenic chelates of industrial origin such as nitrilotriacetic acid (*NTA*) and ethylenediamine tetraacetic acid (*EDTA*) (Stoveland *et al.*, 1979; Knepper, 2003; Ridge and Sedlak, 2004). Unbiodegraded residues of these compounds can then complex with metals and so be unavailable for adsorption by the activated sludge flocs, such that they are retained in solution and arise in the effluent; it has been reported that most of the soluble metal in wastewater is complexed with organic ligands rather present in the free, ionic form (Lawson *et al.*, 1984a; Lawson *et al.*, 1984b; Lawson *et al.*, 1984c). The complexation then determines the speciation and solubility of the metal, and so its mobility and bioavailability in the environment (Sterritt *et al.*, 1985).

6.3 Complexation capacity and stability constant

The speciation of a metal, M, in solution can be represented by the equilibrium (Neubecker and Allen, 1983):

$$M + xL \leftrightarrow MLx \quad \textbf{(6.1)}$$

The stability constant, K, is then given by:

$$K = \frac{[ML_x]}{[M][L]^x} \quad \textbf{(6.2)}$$

where ML_x represents the concentration of the bound metal (mol l^{-1}), M the free metal subtracted from the total metal present (mol l^{-1}), L the concentration of available binding sites (g l^{-1}) and x the stoichiometric ratio. A wide variety of methodologies can be applied to determine the complexation capacity and binding sites (Neubecker and Allen, 1983). Among these, electrochemical techniques such as anodic stripping, voltammetric and differential pulse polarographic (DPP) methods have been the most widely employed (Comte *et al.*, 2008; Morlay *et al.*, 1999; Morlay *et al.*, 2000; Savvaidis *et al.*, 2003).

Removal efficiencies by biotreatment processes of metals vary widely (Chapter 2) and depend on metal speciation and complexation capacity. Metals which are largely complexed by soluble organic ligands may only be removed if these complexes dissociate to form species which have a higher affinity for the biomass (Lester, 1987). The affinity of activated sludge biomass flocs is not well characterised, though considerable attention has been devoted to characterisation of bacterial extracellular polymers (Rudd *et al.*, 1983; Rudd *et al.*, 1984b; Rudd *et al.*, 1984a; Cheng *et al.*, 1975). Although within the past 20 years, much research has been conducted on metal biosorption by activated sludge, few have focused on the stability constants either for biomass or soluble ligands. Different affinities of the extracellular polymers for metals have been reported (Table 6.1). Rudd *et al.*, (1984b) have shown Cu-polymers stability constants to be higher than those for Cd and Ni: Cu>Ni>Cd. Consequently, Cu

may dissociate from its soluble complexes to be removed by association with the biomass flocs. Ni, which has similar affinity for the soluble phase to Cu (Cheng *et al.*, 1975) but a weaker affinity for the biomass flocs (Table 6.1), appears to be removed to a lesser extent: 68% (±25) *vs* 46% (±60) for Cu and Ni respectively (Lester, 1987; Chapter 2). However, although Cd appears to have a weaker affinity for biomass, it has been found to be removed to a slightly greater extent than Ni (62% ±52). In the literature, different affinities orders have been reported (Brown and Lester, 1982a; Rudd *et al.*, 1984b; Cheng *et al.*, 1975; Dugan and Pickrum, 1972) but all have identified Ni as having the weakest affinity for biomass. Lawson *et al.* (1984a) obtained a range of log K values for Cu and Ni at different SRTs; although there is an increased affinity with SRT, it is not significant showing that there is a certain consistency in the affinity of biomass for the metals regardless the operational conditions.

Table 6.1 Conditional stability constants of metal-activated sludge flocs

Metal	log K		Conditions	Reference
	Biomass	EPS		
Cd	4.77-6.52	-	pH 7	Rudd *et al.*, 1983
	5.0-7.0*	4.7-5.0	pH 7	Rudd *et al.*, 1984a
	-	5.16	pH 7	Rudd *et al.*, 1984b
	3.8-4.6	4.2**	pH 7	Guibaud *et al.*, 2003
	-	3.7-5.0	pH 6-8	Comte *et al.*, 2008
Cu	6.71-8.32	-	pH 7	Rudd *et al.*, 1983
	5.5-7.6*	4.6-6.8	pH 7	Rudd *et al.*, 1984a
	-	7.69	pH 7	Rudd *et al.*, 1984b
	5.1, 6.1, 5.8, 6.7	-	SRT=3, 6, 9, 12	Lawson *et al.*, 1984a
	3.0-4.4	3.6**	pH 7	Guibaud *et al.*, 2003
	-	3.2-4.5	pH 4-8	Comte *et al.*, 2008
Ni	4.69-7.50	-	pH 7	Rudd *et al.*, 1983
	4.0-6.2	4.6-6.3	pH 7	Rudd *et al.*, 1984a
	-	5.49	pH 7	Rudd *et al.*, 1984b
	4.6, 6.2, 5.4	-	SRT=3, 6, 12	Lawson *et al.*, 1984a
Pb	3.2-4.1	3.6**	pH 7	Guibaud *et al.*, 2003
	-	3.9-5.7	pH 4-8	Comte *et al.*, 2008

* Measured under sludge age of 12 to 3 days; ** average value; (-) not specified

Like Ni, Pb has been found to display a higher tendency to associate with soluble organic ligands (non-settleable solids) than with biomass (Brown and Lester, 1982a; Chen *et al.*, 1974). Nevertheless, Pb has been found to be removed at efficiencies of 74% (±30) – higher than those reported for Cu (Chapter 2). Zn was found to be adsorbed onto readily settleable particulates (Chen *et al.*, 1974). Its affinity for organic ligands is weaker than that exhibited by Cu and being Zn removed at a similar rate of 68% (±25). This metal, like Cu, would be expected to be removed by association with biomass flocs. The estimation of Cr affinity to ligands is complicated by its oxidation state (Fukushima *et al.*, 1995), and removal efficiency is also affected. Cr normally enters the treatment plant in the hexavalent form (Cr^{6+}), but the trivalent form chromium (Cr^{3+}) is more efficiently removed by adsorption to the suspended solids. However, its oxidation state varies with pH (Fukushima *et al.*, 1995).

Comte *et al.*, (2008) found metal-sludge affinity to be unaffected by pH, though Pardo *et al.,* (2003) amongst others (Table 6.2) reported different orders of affinity depending on pH. Several authors reporting on metal uptake as a function of pH have predicted different stability trends for organo-metal complexes depending on the metal ion and the complexing agents studied (Ozdemir *et al.*, 2003). John *et al.* (1988) observed log K values for metal-humic acid to increase not only with pH but also with humic acid concentration. Activated sludge solids are negatively charged, facilitating its binding to positively charged metal ions (Bux and Kasan, 1994). Therefore, the competition of metal ions for ligand or biomass binding active sites is highly dependent on the solution pH (Hammaini *et al.*, 2007). In most observed studies, metal uptake by the biomass increases with increasing pH and reaches a maximum beyond which metal uptake decreases, suggesting that biosorption is ruled by ionic attraction (Pardo *et al.*, 2003). At low pH values the inactivated cell surface becomes more positively charged, reducing the attraction between metal ions and functional groups on the cell wall. Conversely, when the pH increases the cell surface becomes more negatively charged and biosorption is favoured (Volesky and Holan, 1995; Wong *et al.*, 1993; Sadowski, 2001; Gardea-Torresdey *et al.*, 1990) until an optimum maximum pH is reached.

Several optimal pH values have been reported, beyond no improved biosorption is observed (Al-Qodah, 2006; Pardo *et al.*, 2003; Hammaini *et al.*, 2007).

Table 6.2 Conditional stability constants (log K) of metal-organic ligand

Ligand	Cd	Cr	Cu	Pb	Ni	Zn	pH	Reference
Fulvic acid	-	-	5	-	-	-	5.5	Iglesias *et al.*, 2003
	-	-	5.29	-	-	-	6.5	
	3.8-5.6*	-	4.9-7.0*	4.9-6.9*	-	-	6.5	Sterritt and Lester, 1984
Humic acid	5.32	-	-	-	-	-	5	John *et al.*, 1988
	5.67	-	-	-	-	-	6	
	5.94	-	-	-	-	-	7	
	-	4.4-5.2**	-	-	-	-	3.47-3.5	Fukushima *et al.*, 1995
Citric acid	1.59	-	3.04	-	2.51	2.30	3.5	Brown *et al.*, 1999
	3.76	-	6.55	-	5.80	5.20	6	

*range of values from different analytical method; **depending on oxidation state; (-) not specified

The wide variation in log *K* values reported in the literature (Table 6.1; Table 6.2) relate to widely ranging experimental conditions of pH, temperature, ionic strength and ligand concentration – as well as and method of determination – making the comparison difficult. Morever, the differing chemistries of the organic ligands, with their own polyfunctional nature, means that metal binding characteristics also differ (Brown *et al.*, 1999).

A minor study was conducted at the MBR plant at Cranfield University WwTW to evaluate the performance of a hollow fibre membrane module with respect to metals removal, and data compared to that recorded for the conventional activated sludge pilot plant (Chapter 5) and reported in the literature (Chapter 2).

6.4 Experimental work

Four days of sampling was carried out on MBR pilot plant installed at Cranfield University treatment works (WwTW) (Chapter 9). Samples of influent and permeate were taken in the morning and afternoon to evaluate metals loading influent on the WwTW. Sampling and analysis followed protocols previously identified for the CAS (Chapter 5). Samples were taken during evaluation of flux and aeration criticality (Chapter 9) under operating conditions considered to representative of hollow fibre module MBR operation, approximately 15 l m^{-2} h^{-1} and 0.48 m^3 h^{-1} m^{-2} for the critical flux and aeration determination test, respectively. The immersed HF module used during this study was *S2* (Chapter 9).

Samples of influent, biomass and permeate were taken daily for routine wastewater quality analysis to assess the performance of the pilot plant with respect to aerobic carbonaceous removal and nitrification (Table 6.3). The analyses performed were: mixed liquor (volatile) suspended solids (MLSS and MLVSS), capillary suction time (CST), chemical oxygen demand (COD), ammonia (NH_4^+-N) and nitrate (NO_3^--N), all measured according to the standard methods (APHA, 1998). Other parameters such as pH and conductivity were also monitored. Throughout the study, the MLSS concentration was held between 6-7 g l^{-1} at an HRT and SRT of 14 hours and 44 days, respectively, and the system operated under normal operation achieving more than 90% of efficiency removal for both COD and ammonia.

Table 6.3 Wastewater and biomass characteristics

Parameter	Average value (±SD)
COD, mg l^{-1}	296.0 (±104.0)
NH_4^+-N, mg l^{-1}	38.1 (±13.1)
NO_3^--N, mg l^{-1}	3.6 (±3.9)
pH	7.9 (±0.3)
Conductivity, μS	799.0 (±76.6)
MLSS	6.4 (±0.4)
MLVSS	5.7 (±0.4)
CST	43.5 (±8.3)

6.5 Results

Metal influent concentration and overall removal efficiency were vagarious (Figure 6.1; Table 6.4), but generally increasing during the afternoon reflecting the R&D activities conducted on campus during the day.

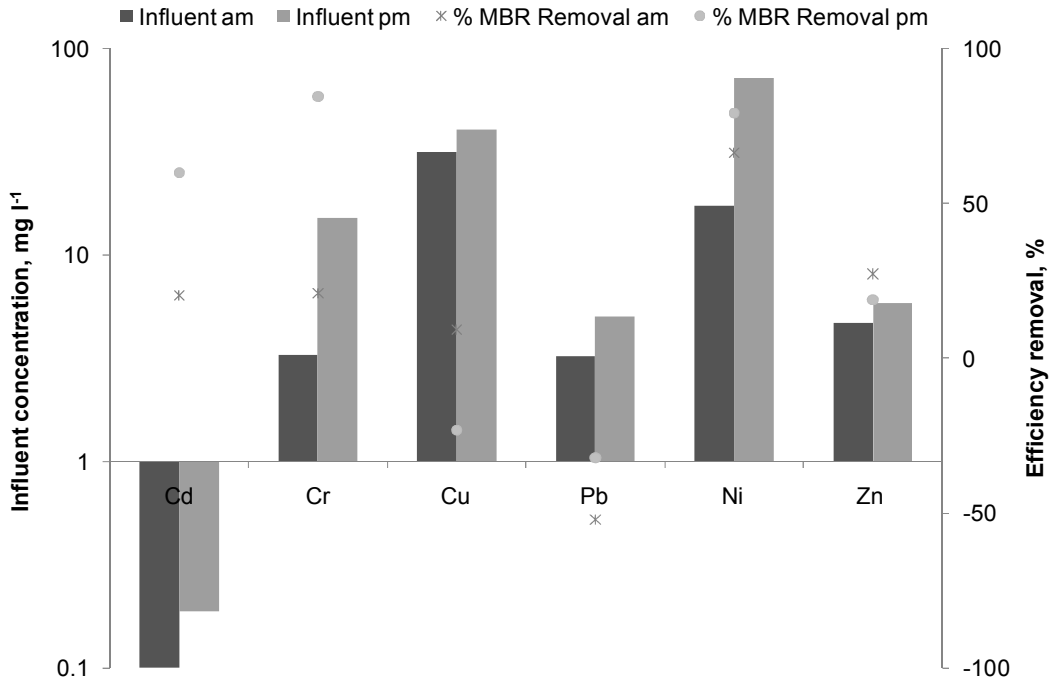

Figure 6.1 Diurnal trends in influent total concentration and removal efficiency

The effluent levels for the most abundant metals (Cr, Cu, Ni and Zn) were in the range 2-28 μg l^{-1} with daily removals ranging from -6.9 to 72.6%. Cd and Pb were both detected at lower levels than reported previously (Chapter 2, Table 2.5) with commensurately high scatter of data reflecting their low detection levels. This would appear to be at odds with the observations of Rossin *et al.*, (1982). The authors found that at higher influent concentration of Cd, Cr, Cu, Ni, Pb and Zn, the removal efficiencies are higher possibly as a result of a more uniform distribution of metal species leading to higher and more consistent removals (Rossin *et al.*, 1982).

Table 6.4. Mean and standard deviation (% SD) MBR toxic metal influent concentration (μg l^{-1}) and removal efficiencies (%), Cranfield University MBR pilot plant

	Cd	Cr	Cu	Pb	Ni	Zn
Mean Concentration	0.2	9.1	36.0	4.2	44.7	5.3
% SD	48.4	74.0	21.5	46.9	120.1	30.5
Mean % Removal	40.2	52.8	-6.9	-42.1	72.6	23.0
% SD	141.5	79.1	-1150.2	-94.6	48.2	407.7

As previously reported by Santos and Judd, (2010) (Chapter 2), Cu and Zn are ubiquitous in wastewater, and usually detected at concentrations higher than 100 μg l^{-1} being removed at rate higher than 70%, much higher than the levels detected in the current study (5.3 and 36.0 μg l^{-1} for Zn and Cu, respectively) but comparable to the Cu levels reported by Santos *et al.*, (2010) (Chapter 5, Table 5.4). As already stated, according to the log K values found in the literature (Table 6.1; Table 6.2), the affinity of both Cu and Zn for organic ligands is weaker than for biomass, so such that these metals would generally be expected to be better removed. However, during this study, Cu and Zn were not removed to the same extent usually reported (Chapter 2).

According to the reported data Cr and Ni have demonstrated the most consistent removal efficiencies with mean removals lower than the mean

literature value in the case of Cr (83 *vs* 53%), and higher for Ni (73 *vs* 64%). No data for Cr affinity for biomass has been reported in the literature. However Cr affinity for soluble ligands (humic acid) is similar to Cd, and Cd has an affinity similar to biomass as Cu. Therefore, since Cr is removed at higher rate than Cu (Chapter 2), it is likely that Cr has a stronger affinity for biomass than for soluble ligands, accounting for its relatively high removal efficiency. Ni, although having an affinity for organic ligands generally greater than that for biomass (Table 6.2), appears to have been more significantly removed than Cu which is present at a similar mean concentration and with a greater reported affinity for biomass (Table 6.4).

Although EPS is likely to have the major role on metal removal, it is possible that other components, such as the anthropogenic chelating agents which may arise from research activities on the University campus, affect metal uptake by activated sludge enhancing metal solubility such as Cu and Zn.

In Chapter 5, Cu and Zn removal by membrane filtration at different pore sizes was evaluated, the membrane being challenged with mixed liquor held at approximately 3.6 g l^{-1} by an HRT and SRT of ~6 h and ~4.3 days respectively. The efficiency removal was calculated considering the mixed liquor as the mass balance only took into account the membrane filtration unit and not the biological treatment. Therefore overall removal efficiencies (Table 6.5) are greater than those obtained for the Cranfield study and reported in the literature.

Table 6.5 Removal efficiencies of an activated sludge pilot plant with membrane filtration unit (Chapter 5)

	Removal efficiency, %		
	0.01 µm	0.08 µm	0.40 µm
Cu	91.3	92.2	86.8
Zn	97.7	97.6	97.5

One of the advantages of the MBR systems is the ability to operate with uncoupled HRT and SRT, and hence high MLSS concentration (Judd, 2008). At higher MLSS concentration, the EPS and the soluble microbial products (SMP) concentration are both higher, with the latter providing more available soluble ligands to complex with metal. As such MBR systems may be deleterious to metal removal if increased particulates removal is substantially countered by metals solubilisation.

6.6 Conclusion

The complex nature of the wastewater makes it difficult to define the precise speciation form of the metals present. Metal solubility is greatly affected by operation, physicochemical and biological parameters and it is thus only possible to estimate solubility (Lester, 1987). Also, the ligand-metal interaction in natural systems is very complicated due to the heterogeneous nature of the organic ligands and competition between the different metals (Brown *et al.*, 1999). Metals are thus removed to different extents due to multifarious and often competing factors influencing metal uptake by the biomass.

Metals with a stronger affinity for organic ligands, as reflected in higher log K values, would be expected to be less significantly removed. However, correlation of measured removal with literature log K values is poor. Moreover, no pattern in removal efficiency has been evident for either metal type or chemical behaviour although differences in removal efficiency may reflect the different chemical forms of each metal with different solubility at the influent pH of ~7.2.

During the studies carried out at Cranfield and in the North West (Chapter 5), the plant operation parameters such as SRT, HRT and MLSS concentration had some impact on metals removal. However, the influences on metals removal are multifarious and complex, with the key operating determinants of SRT and HRT impacting both on MLSS concentration but also on metals and organic ligand speciation, and thus complexation which may be linked to parameters such as effluent COD and suspended solids (Chapter 2; Chapter 5). Although metal removal was enhanced by replacing the secondary sedimentation tank by membrane filtration unit, when operating at larger scale and close to representative MBR operational conditions, MBR technology may offer little benefit with respect to metals removal.

The removal efficiencies followed the sequence Ni>Cr>Cd>Zn>Cu>Pb, and were lower than those found in the literature where the sequence is Cu≥Cr>Zn>Cd>Pb>Ni (Chapter 2). Given the mercurial nature of metals

removal by biotreatment resulting from their apparently highly labile nature, it is questionable that the low EQS levels set by legislation can be considered realistic.

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7 FATE AND REMOVAL OF PERMETHRIN BY CONVENTIONAL ACTIVATED SLUDGE TREATMENT

Ana Santos[1], Ruben Reif[2], Peter Hillis[3] and Simon J. Judd[1]

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[1]Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK
[2]Department of Chemical Engineering, Group of Environmental Engineering and Bioprocesses, University of Santiago de Compostela, Santiago de Compostela, Spain
[3]United Utilities, Great Sankey, Warrington, Cheshire, WA5 3LW, UK

Abstract

The fate and removal of permethrin during conventional wastewater treatment was evaluated at pilot plant scale at different MLSS (mixed liquor suspended solids) concentrations, and hence different solids retention times, SRT. At feed concentrations of 0.3-0.9 $\mu g\ l^{-1}$, the permethrin was removed by primary treatment at an efficiency rate of 37%, similar to previous reported data, and by 40 to 83% for secondary treatment, decreasing with decreasing SRT. Comparable ranges, from 37 up to 98%, have been reported for micropollutants with similar physicochemical properties to permethrin, such as galaxolide and tonalide. Little difference in removal was noted between the medium and low MLSS concentrations trials, the main difference in treated effluent permethrin concentration arising on changing from high to medium MLSS levels. This was attributed to the limited acclimatisation period employed in these two trails, leading to higher levels of soluble organic matter in the treated water with which the permethrin appeared to be associated.

7.1 Introduction

Under the EU Water Framework Directive (2000/60/EC), permethrin is classified as a potential main pollutant (European Commission, 2000). The Environmental Quality Standards (EQSs) are provided as threshold values below which no adverse impact is expected on either human health or the environment. For permethrin, the EQS was set to a value of 0.01 $\mu g\ l^{-1}$ at the 95%ile (SEPA, 2004).

Permethrin (3-phenoxybenzyl (1RS)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclpropanecarboxylate) has four isomers, *cis*- and *trans*-isomers, both have two optical isomers. It is a neurotoxin widely used in agriculture, domestic environments and in healthcare as a pest control agent, ranging from head lice to Dengue fever. Its toxicity is highly dependent on stereochemical structure, the *cis*-isomer being more toxic (Baser *et al.*, 2003), and its adverse impacts in the environment are well documented (US EPA, 2009; Kamrin, 1997). It can enter the aquatic environment by urban and agricultural run-off, industrial discharges, leachates from landfill site, atmospheric deposition and wastewater treatment works effluents or storm overflows (Scrimshaw and Lester, 1996). Once in the aquatic environment, permethrin has a significant impact as it destroys both the quality and quantity of insects and invertebrates in the ppb range (Bacey *et al.*, 2005), though there is no evidence of endocrine disruption activity and its possible carcinogenicity is currently unproven conclusively (US EPA, 2009; NPIC, 2009).

Removal of micropollutants from wastewater is largely dependent on their physicochemical properties and on the nature of the treatment process involved (Meakins *et al.*, 1994). Permethrin is a non-polar hydrophobic organic micropollutant of low water solubility ($5.5x10^{-3}$ mg l^{-1}), high organic carbon affinity (K_{oc}=16.4-550 l g^{-1}) and strong lipophilic character (log K_{ow}=6.1, K_{ow} being the octanol-water partition coefficient). As such, its physical chemistry strongly resembles the polycyclic musk (PCM) fragrances galaxolide and tonalide (Table 7.1). It is only slightly higher in relative molecular mass M_W (391

vs 244-258) but is in the same range of K_{oc} (6.1 *vs* 4.6-6.6) and K_d, the sludge-water distribution coefficient. Permethrin thus tends to adsorb onto soil, biota or, within a wastewater treatment process, the wastewater bioreactor flocculant solids or flocs (Laskowski, 2002). Since permethrin is not very mobile in water and readily broken down by microorganisms (Kamrin, 1997), it is unlikely to leach to groundwater.

Table 7.1 Physico-chemical properties of permethrin and PCMs

Application	Name	M_w	s	log K_{ow}	log K_d	
					Primary sludge	Secondary sludge
Polycyclic musk fragrances	Galaxolide	258.4	1.8	5.9-6.3	3.7	3.4
	Tonalide	258.4	1.3	4.6-6.4	3.7	3.3
Pesticides	Permethrin	391.3	$5.5x10^{-3}$	6.1	3.5	3.9

M_w: Molecular weight in g mol^{-1}; s: solubility in water in mg l^{-1}; K_{ow}: octanol-water partition coefficient; K_d: sludge-water distribution coefficient in l kg^{-1} SS (Laskowski, 2002; Kupper *et al.*, 2006; Suárez *et al.*, 2008).

Reported data for permethrin removal by classical biotreatment are limited, and plant operating data not often included. A comparison with available data for the two PCMs galaxolide and tonalide (Table 7.2) reveals that, in all cases, removal efficiency is variable and does not correlate with settled sewage influent concentration. For PCMs, the removal efficiencies reported for conventional activated sludge (CAS) processes range from as low as 37 up to 98%, whilst for permethrin the reported removal values have been between 70 and 94%. Whilst their removal may be through a combination number of mechanisms, such as biodegradation, adsorption, volatilization or hydrolysis, the properties outlined in Table 7.1 suggest that for permethrin, PCMs and other organic lipophilic micropollutants with high adsorption coefficient, removal is primarily through adsorption onto sludge solids. Biodegradation, on the other hand, has been reported to be limited (Bester, 2004), implying that significant amounts of these compounds may persist in the aquatic environment.

Table 7.2 Reported micropollutant removal under various conditions of influent concentration and bioreactor hydraulic and solids residence time (HRT and SRT respectively)

Micropollutant	Influent, $\mu g\ l^{-1}$	Removal efficiency,%	HRT, hours	SRT, days	Reference
Permethrin	0.12	88	-	-	Gómez *et al.*, 2007
	0.14	92	8	16	Kupper *et al.*, 2006
	-	94	-	-	Plagellat, 2004
	-	70-90	-	-	Abram *et al.*, 1980
Galaxolide	1.94	37	8	8-10	Bester, 2004
	4.82	70-85	-	-	Carballa *et al.*, 2004
	3.42	77	8	16	Kupper *et al.*, 2006
	0.02	90-98	-	-	Horii *et al.*, 2007
	7.03	72	-	-	Smyth *et al.*, 2008
	3.48	53	15	-	Lee *et al.*, 2010
	1.59	68	6	>150	Reif *et al.*, 2010[a]
Tonalide	0.58	37	8	8-10	Bester, 2004
	2.51	75-90	-	-	Carballa *et al.*, 2004
	1.33	76	8	16	Kupper *et al.*, 2006
	0.15	72-94	-	-	Horii *et al.*, 2007
	0.77	56	15	-	Lee *et al.*, 2010
	0.70	75	6	>150	Reif *et al.*, 2010 [a]

[a] see Appendix B; (-): not specified

The extent of adsorption onto the flocs depends both on the micropollutant physico-chemical properties and the floc surface (Dionisi *et al.*, 2008). Extracellular polymeric substances (EPS), a key bioreactor mixed liquor component, have been reported as contributing to adsorptive removal of transitional metals and organic micropollutants (Suárez *et al.*, 2008; Chapter 2), and the hydrophobic component of EPS may be expected to contribute to the removal of hydrophobic micropollutants such as permethrin. However, the biochemical nature of the mixed liquor is dependent wastewater treatment operating parameters, and most significantly the sludge retention time (SRT)

which impacts on the microorganism growth and final effluent quality. Studies have demonstrated that a high SRT enhances removal and degradation of non-polar hydrophobic organic micropollutants by allowing the more slowly growing bacteria to establish, including more diverse biocoenosis such as nitrifying bacteria for which it is claimed may able to degrade a number of micropollutants (Clara *et al.*, 2005). Short SRTs (<8 days) lead to the removal of these bacteria from the system, such that biodegradation is less significant and adsorption onto the sludge is more important (Jacobsen *et al.*, 1993). For SRTs greater than 8 days, available data indicates removal efficiencies above ~64% (Table 7.2) are attained. It is clearly of interest to establish the impact of both SRT and, more specifically, mixed liquor suspended solids (MLSS) concentration on permethrin removal efficiency. The reported study concerns removal efficacy for permethrin through operation of a CAS plant at the pilot-scale at MLSS concentrations between 2.7 and 5.4 g l^{-1}.

7.2 Material and Methods

The pilot plant employed for the study is described elsewhere (Chapter 5). The plant (Figure 7.1) was initially seeded with mixed liquor from a full-scale activated sludge plant. Acclimation for four weeks followed seeding, after which time the experimental sampling trial commenced. Each set of operating conditions was maintained for a period of two weeks after which the MLSS concentration was adjusted downwards, decreasing the SRT. The sampling trial was completed in three one-week trials – high, medium and low MLSS trial (Table 7.3) – with the sampling being performed on the second week of the two-week period.

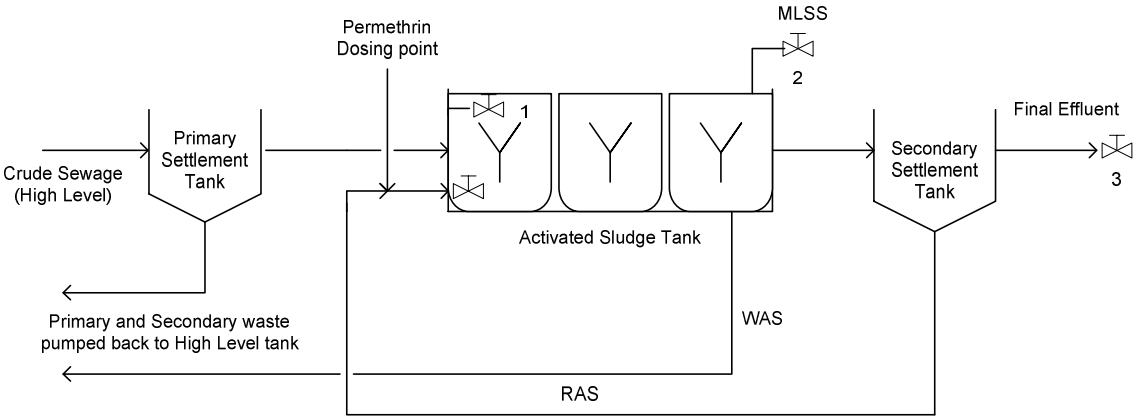

Figure 7.1 Activated sludge pilot plant with sampling points 1: Influent; 2: Mixed Liquor Suspended Solids (MLSS); 3: Return Activated Sludge (RAS); 4: Final Effluent

Table 7.3 Operational conditions and efficiencies removal (weekly trial average±SD)

	High MLSS	Medium MLSS	Low MLSS
Activated sludge tank			
MLSS, mg l^{-1}	5061 (±377.4)	3400 (±234.7)	2685 (±333.2)
HRT, hours	6	6	6
SRT, days	8	4.3	3.6
DO, mg l^{-1}	7.5 (±0.9)	8.6 (±0.5)	8.3 (±0.7)
Redox potential, mV	94.3 (±12.7)	65.9 (±14.2)	74.5 (±13.5)
Temperature, °C	15.8 (±1.9)	14.5 (±1.8)	14.0 (±1.3)
pH	7.0 (±0.4)	7.0 (±0.3)	6.8 (±0.4)
Efficiency removal, %			
TSS	73.7 (±4.5)	76.3 (±5.3)	63.6 (±13.5)
BOD	95.1 (±0.6)	92.1 (±5.0)	88.6 (±4.2)
sBOD	94.9 (±1.1)	98.2 (±1.2)	96.6 (±2.8)
COD	79.5 (±6.3)	87.3 (±1.1)	82.1 (±5.0)
sCOD	80.6 (±8.9)	81.0 (±4.6)	85.4 (±4.8)
$N\text{-}NH_4$	97.9 (±0.7)	98.3 (±0.6)	98.5 (±0.1)

Sampling points were as indicated in Figure 7.1 for the pilot plant treating influent dosed with 0.8-1 µg l^{-1} from a permethrin stock solution which was freshly prepared daily. The influent flow was maintained at around 300 l h^{-1} to provide a hydraulic residence time (HRT) of 6 hours, and the return activated sludge (RAS) ratio was set at 1:1 with reference to the influent flow. Throughout

the trials, samples were taken at 09:00 and at 13:00 each day from the settled sewage influent, MLSS, RAS and final effluent streams for both the target micropollutant and wastewater quality analyses to assess performance with respect to permethrin and organic carbon removal, and nitrification.

7.2.1 Permethrin sample preparation and extraction

The dissolved phase extraction for MLSS, RAS, and influent samples was undertaken using pre-conditioned *Chromabond C18ec* extraction columns (6 ml *per* 1000 mg) solid phase extraction (SPE) cartridge (Macherey-Nagel, Dueren, Germany) and a vacuum manifold (Agilent Technologies, Manchester, UK) connected to a vacuum pump (KNF Neuberger GmbH Freiburg, Germany). The SPE cartridges were pre-conditioned with 5 ml methanol 'Distol' grade (Fisher Scientific, Loughborough, UK) and 5 ml ultra pure (18.2 MΩ) water (ELGA, High Wycombe, UK). Silanised glass wool (VWR, Lutterworth, UK) was used as a pre-filter in the SPE cartridge. After loading the sample, the cartridges were washed with 1 ml ultrapure water and dried for 1 hour under vacuum prior to storage in a sealed plastic bag (Fisher Scientific, Loughborough, UK) and, along with the GF/C filter, frozen to preserve the samples until the analyses were performed. For the final effluent, the total phase was extracted following the same method as described for the dissolved phase extraction.

The SPE cartridges were eluted with sequential 20 ml portions of diethyl ether 'Distol' grade (Fisher Scientific, Loughborough, UK) into a glass vial before evaporating with oxygen free nitrogen (BOC, Manchester, UK). The residue was then dissolved in 0.5 ml 'Distol' grade hexane (Fisher Scientific, Loughborough, UK) and the vial sealed. Analysis were conducted with a standard split-less 2 μl injection on a model *Autosystem XL* gas chromatograph (GC) and *TurboMass Gold* mass spectrophotometer (MS) (Perkin Elmer, Beaconsfield, UK) with a 30 m x 0.25 mm i.d. x 0.25 nm film thickness 5% phenyl – 95% dimethyl polysiloxane capillary column (Phenomenex, Macclesfield, UK) using calibration

standards of *cis*- and *trans*-permethrin at 0.25 and at 0.75 mg ml^{-1} respectively (Sigma-Aldrich, Gillingham, UK).

7.2.2 Wastewater quality analyses

Routine wastewater quality analyses were performed on samples taken at the sampling points shown in Figure 7.1 on a daily basis. Analyses included total and soluble biochemical oxygen demand (BOD), total and soluble chemical oxygen demand (COD), total suspended solids (TSS) and ammoniacal nitrogen ($N\text{-}NH_4$) following standard methods (APHA, 1998). Other parameters such as pH, temperature, redox potential and dissolved oxygen (DO), were monitored using a multiparameter *HANNA* instrument *HI 9828* (HANNA, UK).

7.2.3 Mass balance calculations

The permethrin adsorption coefficients, K_d, for primary and secondary sludge provided by Kupper *et al.*, (2006) were used to determine the permethrin concentration adsorbed onto sludge solids (Table 7.1). The amount of permethrin in crude sewage liquid phase for samples was also assumed to be equal to influent liquid phase. For the mass fluxes for permethrin load on the stream (Figure 7.1) were calculated according to the next expression:

$$m = Q_{in}(S + X) \quad \textbf{(7.1)}$$

where m is the mass flux of permethrin (µg day^{-1}) entering or leaving a specific unit of the WwTW, Q is the sum of incoming flows (l day^{-1}), S is the permethrin concentration in the liquid phase (µg l^{-1}) and X is the amount of permethrin estimated to be adsorbed onto the solid phase.

7.3 Results and Discussion

Assuming that the amount of permethrin in the crude sewage is equal to the settled sewage influent, permethrin removal was estimated to be at around 37% in reasonable agreement with removal efficiencies of up to 35% reported by Kupper *et al.*, (2006). Removal of polycyclic musk fragrances of high pK_d values of 10-51% have been reported for the primary treatment stage (Kupper *et al.*, 2006; Carballa *et al.*, 2004; Simonich *et al.*, 2002; Artola-Garicano *et al.*, 2003), increasing to 50-70% when coagulant dosing is employed (Suárez *et al.*, 2008).

Removal efficiency during secondary treatment was found to decrease with decreasing MLSS concentration, and hence also with decreasing SRT (Table 7.4), with overall removal decreasing from 89 down to 65%. The data imply removal efficiency values of 83.3, 44.3 and 40.4% for the highest, medium and lowest MLSS levels. This pattern*, i.e*. with only a marginal change in percentage removal from the second to the third trial, may reflect the significantly reduced acclimation period employed for these two trials (one week) compared with the substantially longer one prior to the first trial (five weeks). A review of the final effluent data reveals the soluble COD (sCOD) concentration, representing a reasonable indication of EPS levels, increases by 43% between the first and the second trial but by only 6% between the second and third trials (Table 7.5). There is therefore some indication that the concentration of permethrin in biotreatment process effluents may more close follow the sCOD level than that of the suspended solids, notwithstanding the fact that permethrin is expected to be associated with solids.

During conventional biological treatment, for respective settled sewage influent concentration of 3.04-5.80 and 1.15-1.71 $\mu g\ l^{-1}$ for galaxolide and tonalide, removal rates of 75-78% for galaxolide and tonalide have been reported when operating at an SRT of 16 days (Kupper *et al.*, 2006). Lower percentage removal rates of 30-40% for galaxolide and 45-50% for tonalide, at influent detection levels of 2.1-3.4 $\mu g\ l^{-1}$ for galaxolide and 0.9-1.7 $\mu g\ l^{-1}$ for tonalide have also been reported (Carballa *et al.*, 2004). Insufficient information was

provided in this case to determine the comparative impact of operation conditions or influent concentration on removal efficiencies.

From Table 7.2 it can be concluded that, for tonalide and galaxolide, the SRT above 8 days enhance the overall removal of organic micropollutants sufficiently to allow a minimum removal efficiency of 37 up to 98%.

Table 7.4 Permethrin removal data

Trial	MLSS, g l^{-1}	SRT, days	Influent, µg l^{-1}	Efficiency removal (%)		
				Primary	Secondary	Overall
High	5.4	8	0.3 (±0.16)	38.4 (±15.7)	83.3 (±8.01)	88.9 (±7.32)
Medium	3.4	4.3	0.9 (±0.23)	36.8 (±12.6)	44.3 (±8.82)	65.4 (±1.44)
Low	2.7	3.6	0.6 (±0.46)	na	40.4 (±28.0)	na

na: not available

Table 7.5 Final effluent data

Trial	Acclimation period, week	sCOD, mg l^{-1}	TSS, mg l^{-1}	Concentration, µg l^{-1}
High	5	26.8 (±6.72)	21.0 (±1.73)	0.1 (±0.02)
Medium	1	38.2 (±7.89)	21.8 (±1.71)	0.4 (±0.02)
Low	1	40.6 (±12.9)	30.4 (±9.32)	0.3 (±0.12)

There is evidence that HRT, along with other operational conditional such as temperature, pH and redox conditions, may affect organic micropollutant removal, with lower removals at reduced HRTs (Tauxe-Wuersch *et al.*, 2005). Kupper *et al.* (2006) reported permethrin removal of 96% when operating at an HRT of 8 hours longer than that used by the current study with removal rates between 40.4-83.3% at 6 hours retention time (Table 7.2). As for the PCMs, anecdotal evidence suggests HRT may influence the removal efficiency but in the absence of reported data on other operating conditions, the degree of infiltration and sampling protocols makes it difficult to be precise in this regard.

7.4 Conclusions

The occurrence and removal of permethrin in a conventional activated sludge process has been investigated at pilot-plant scale at different MLSS concentrations whilst maintaining appropriate removals efficiency of the conventional wastewater quality determinants of TSS (71.1±6.9%), COD (83.0±4.0%), BOD (92.0±3.3%) and N-NH_4 (98.2±0.3%). From these trials permethrin had different behaviour:

- The recorded removal efficiency for primary treatment of 37% on average was similar to previously reported data (Kupper *et al.*, 2006).

- The removal efficiency for secondary treatment (conventional activated sludge) ranged from 83 down to 40% on decreasing from the highest to the lowest MLSS concentration, with SRT concomitantly decreasing from 8 to 3.6 days. Removal was consistent with the generally recognised mechanism for hydrophobic organic micropollutants (*i.e*. high K_{ow}, low solubility and low biodegradability) of adsorption onto the sludge solids, with similar results having previously been reported indicating the benefit of operating at SRTs above 8 days (Clara *et al.*, 2005; Cirja *et al.*, 2008).

- The overall permethrin removal across the combined primary and secondary stages was 65-89%. Reported removals for organic micropollutants having similar properties range from 37 to 98% (Kupper *et al.*, 2006; Bester, 2004; Carballa *et al.*, 2004; Horii *et al.*, 2007; Smyth *et al.*, 2008; Lee *et al.*, 2010; Reif *et al.*, 2010).

- Acclimation period may have a significant impact on removal, with some evidence of permethrin being associated with increased soluble COD in the effluent. Soluble COD has been associated with soluble EPS, which arises when the system is perturbed.

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8 CRITICALITY OF FLUX AND AERATION FOR A HOLLOW FIBRE MEMBRANE BIOREACTOR

Hèctor Monclús[1], Sebastian Zacharias[2], Ana Santos[2], Marc Pidou[2] and Simon J. Judd[2]

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[1]Faculty of Sciences, University of Girona, Girona, Spain
[2]Center for Water Science, Cranfield, University, Cranfield, Bedfordshire, UK

Abstract

A three-module microfiltration (MF) hollow fibre (HF) membrane cassette has been evaluated for treating municipal wastewater by an immersed membrane bioreactor (iMBR) based on a pilot-scale plant. The flux-step method, classically used to identify the critical flux, was compared with an aeration-step method conducted at the identified critical flux of 14.5 l m^{-2} h^{-1}. It was found that the permeability of the central module was found to be higher, since the air stream imparted to the end modules was dissipated because there is no channel formed by the proximity of the neighbouring modules. The aeration-step trials revealed the critical specific aeration demand for both intermittent and continuous aeration regimes to be lower than that applied to the critical flux-step experiments. This implies that the operating conditions identified for critical flux-step experiment are over conservative, corroborating results from previous reports, and that aeration stepping presents a more representative method for identifying sustainable operating conditions.

8.1 Introduction

The immersed membrane bioreactor (iMBR), which combines biological treatment with membrane filtration, has been established for almost two decades (Stephenson *et al.,* 2000). The MBR offers a number of advantages over the classical activated sludge process (ASP), including production of consistently high-quality effluent. The technology can be operated at extended solids retention times (SRTs), thereby reducing the reactor size, increasing the MLSS concentration and reducing the waste volumes generated due to the decreased sludge yield. However, MBR operation is ultimately constrained by membrane surface fouling (Wang *et al.*, 2007; Chu and Li, 2005; Choi *et al.*, 2005) and also membrane channel clogging (Judd, 2008). This leads to a reduction in permeability of the membranes and demands their frequent physical and chemical cleaning to maintain production. Fouling phenomena are extremely complex in MBRs due to the large number of contributing factors, such as like the nature of the membrane (geometry, material type, pore size and size distribution, *etc.*), the biomass (solids concentration, floc size and characteristics, macromolecule concentration and physicochemistry) and the operating conditions (aeration, sludge age, flux) (Judd and Judd, 2006).

Fouling of iMBR membranes in practice is minimised by sub-critical flux operation, through a combination of limiting the flow through the membrane and promoting turbulence by aeration of the membranes, which acts to scour and/or agitate them (Judd and Judd, 2006). Critical flux (J_c) can be broadly defined as the flux, or the flow rate *per* unit membrane area, below which no deposition of foulants takes place (Field *et al.*, 1995). In the “strong” form, J_c is defined as the flux below which the membrane permeability during filtration is the same as that for clean water filtration. It is broadly accepted that this definition is not appropriate to MBRs where membrane fouling takes place even at very low fluxes (Le Clech *et al.*, 2003; Cho and Fane, 2002).

Tests performed to identify the critical flux normally take the form of the classical flux-step test, where the flux is incrementally increased at steps of 2 to 5 l m^{-2} h^{-1} and for periods of 15 to 60 minutes and the transmembrane pressure (TMP) response observed (Le Clech *et al.*, 2003; Howell *et al.*, 2004; Guglielmi *et al.*, 2007). Many authors report a roughly exponential increase in rate of increase in TMP (dTMP/dt, usually referred to as the fouling rate) with the applied flux (Le Clech *et al.*, 2003; Howell *et al.*, 2004; Guglielmi *et al.*, 2007). However, it has also been noted (Le Clech *et al.*, 2003) that the measured critical flux is dependent on the step length, along with other factors relating to the sludge quality.

The key contribution to energy demand in immersed systems is the specific aeration demand for membrane scouring, SAD_m, in Nm^3 h^{-1} air *per* m^2 membrane area (Judd and Judd, 2006). Air is used for biomass floc suspension and circulation, membrane scouring in the case of flat sheet (FS) membranes, and agitation for hollow fibre (HF) membranes. Energy consumption rates as low as 0.62 kWh m^{-3} have been reported on full-scale immersed MBR installations (Garcés *et al.*, 2007) where 41% of the energy consumed was for aeration and comprised 29% for membrane aeration and 12% for process aeration. In the past it has been demonstrated that there is a linear relationship between flux and aeration rate up to a threshold value beyond which no further increase in permeability take place (Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007; Ueda *et al.*, 1997). However, no study of critical aeration demand at a fixed flux has been made.

This pilot study aims to determine the critical flux of a microfiltration (MF) HF membrane using the flux-step method. Further, it aims to determine the critical specific aeration demand ($SAD_{m,crit}$), and the impact of SAD_m and aeration regime on membrane fouling.

8.2 Materials and Methods

The pilot-scale plant comprised a 2.5 m^3 bioreactor with a vertically-mounted cassette fitted with three-module membrane, each providing a surface area of 3.33 m^2. The MF HF modules were of polyvinylidene fluoride (PVDF) with a pore size of 0.1 µm and were 1.4 mm in external diameter (Table 8.1). The cassette was immersed to a depth of 0.5-1.0 m and permeate was extracted using a peristaltic pump. Transmembrane pressure (TMP) was monitored using pressure sensors connected to a dedicated data logger.

The feed was settled sewage from the Cranfield University Wastewater Treatment Works (Table 8.2), and samples of sludge and water were taken at regular intervals. The sludge was sampled for the mixed liquor suspended solids (MLSS) and the mixed liquor volatile suspended solids (MLVSS) content, these being determined by Standard Methods 2540D and 2540E respectively (APHA, 1998). Similarly, standard methods were used to measure the chemical oxygen demand (COD), ammonia (NH_4^+-N), nitrogen oxide compounds (NO_x), and sludge volume index (SVI). The MLSS concentration was held at between 7-9 g l^{-1} throughout the trial, and tests were performed on the three modules individually.

Table 8.1 Membrane and module specification

Description	Value
Type	HF MF
Membrane material	PVDF
Pore size, mm	0.1
Internal fibre diameter, mm	0.9
External fibre diameter, mm	1.4
Fibre length, mm	1500
Dimensions of fibre bundle (LxWxH), mm	169x40x1620
Dimensions of module (LxWxH), mm	400x300x2140
Number of fibres per bundle	517
Fibre separation, mm	1
Bundle separation, mm	20
Packing density, $m^2\ m^{-3}$	293
Bundle area, m^2	3.33
Total effective membrane surface area, m^2	10

Table 8.2 Wastewater characteristics

Parameter	Value
COD, mg l^{-1}	290
NH_4^+-N, mg l^{-1}	35
NO_x^-, mg l^{-1}	0.3
pH	7.6
SVI, ml g^{-1}	116

Two types of test were performed: flux-step and aeration-step. The classical flux-step method was similar to that reported previously (Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007; Bottino *et al.*, 2009). Flux steps were performed at 15 minute intervals at steps of ~5 l m^{-2} h^{-1} up to a maximum flux of around 25 l m^{-2} h^{-1}. The flux-step experiment was used initially to determine the critical flux of all three modules individually. For this trial the modules were operated without relaxation and with continuous aeration at a SAD_m of 0.48 Nm^3 m^{-2} h^{-1}. The

second flux-step experiment was performed on the central module alone with relaxation (9 minutes permeation with 1 minute of relaxation) and with intermittent aeration (10 sec on/10 sec off at a SAD_m of 0.24 $Nm^3\ m^{-2}\ h^{-1}$). In both cases the critical flux was assumed to be the flux at which the fouling rate, dTMP/dt, exceeded a threshold of 0.5 mbar min^{-1}.

Aeration-step experiments were used to determine the $SAD_{m,crit}$ of the membranes under conditions of intermittent and continuous aeration. During this test, the permeation regime was cyclic (15 min on/1 min relaxation) at a constant flux of around 14.5 l $m^{-2}\ h^{-1}$. Each SAD_m step was duplicated, such that each step comprised 30 minutes of permeate extraction in total. The same limiting fouling rate as previously (0.5 mbar min^{-1}) was applied to determine $SAD_{m,crit}$. A standard maintenance clean, or chemically-enhanced backflush (CEB), was employed prior to each test; a 500 mg l^{-1} hypochlorite solution was applied at 5 backflush pulses of 15 seconds duration and a flux of ~55 l $m^{-2}\ h^{-1}$, with around 5 minutes of relaxation time between pulses.

8.3 Results

8.3.1 Critical flux test

8.3.1.1 Module comparison

The fouling rate at a constant SAD_m of 0.48 $Nm^3\ m^{-2}\ h^{-1}$ for all individual modules followed the expected exponential relationship with flux (Figure 8.1), corroborating previously reported correlations (Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007; Bottino *et al.*, 2009), but with no clear inflection at the assumed critical flux J_c. Critical flux was thus arbitrarily taken as the flux corresponding to a fouling rate of 0.5 mbar min^{-1}. Accordingly, the critical flux values of Modules A and B were 16.6 l $m^{-2}\ h^{-1}$ and 17.0 l $m^{-2}\ h^{-1}$ respectively, while it was slightly lower for module C at 12.6 l $m^{-2}\ h^{-1}$. At its peak the permeability of the central module was ~30% more than the module A and ~65% more than module C. Comparing the fouling rates of the three modules revealed that, with the

exception of one anomalous result, the central module had consistently lower fouling rates.

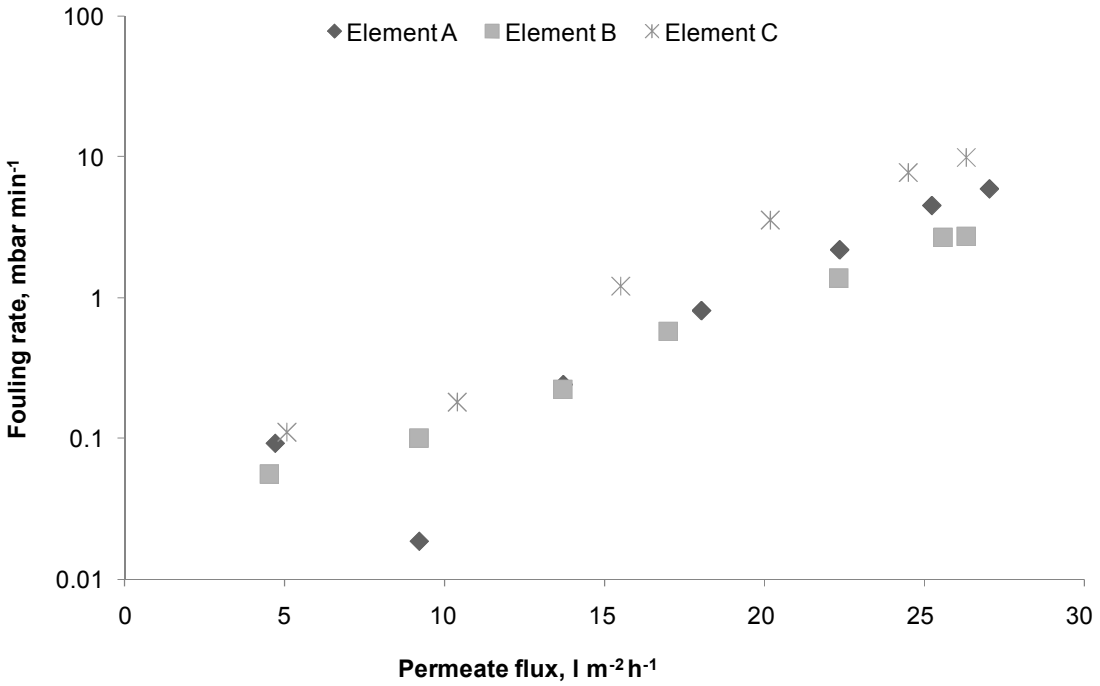

Figure 8.1 Trend of fouling rate for each individual module; continuous aeration without relaxation (at a SAD_m of 0.48 Nm^3 m^{-2} h^{-1})

8.3.1.2 Central module tests

The flux-step experiment was duplicated for the central module. Cyclic permeation was introduced (9 min on/1 min relaxation) along with intermittent aeration (10 sec on/10 sec off) at an overall SAD_m of 0.24 Nm^3 m^{-2} h^{-1}, and the fouling rate measured as before (Figure 8.2). Under these conditions, the J_c of the central module was estimated to be around 14.7±0.5 l m^{-2} h^{-1}. It was also observed that at higher flux, the fouling rate of the module was slightly lower under continuous aeration operation than for intermittent operation.

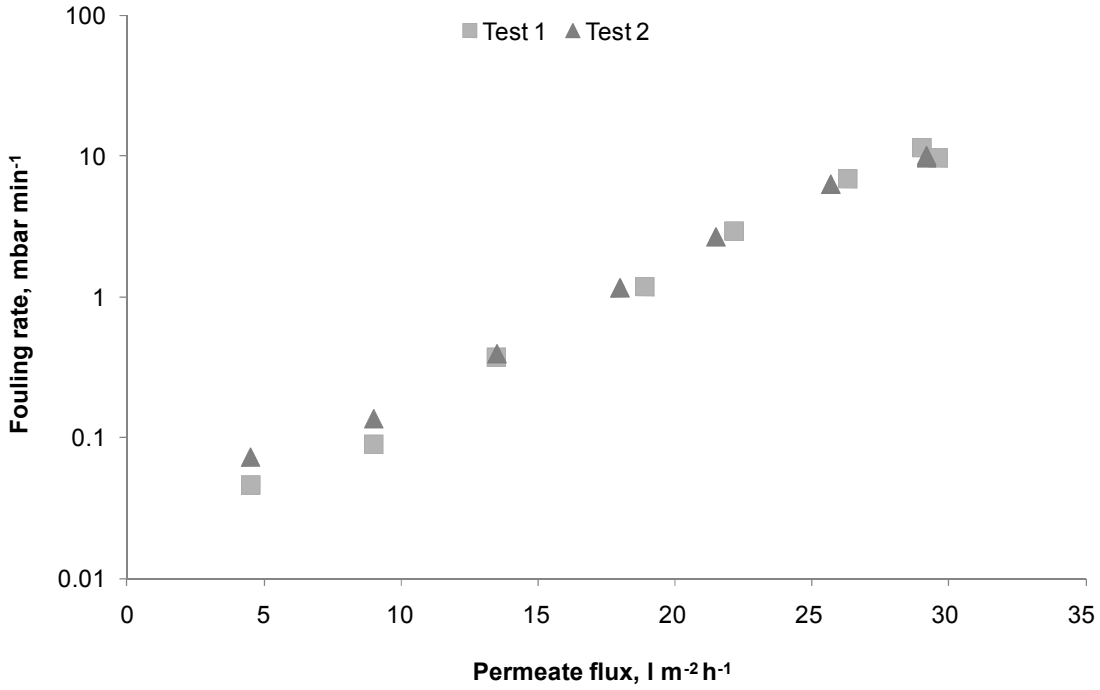

Figure 8.2 Trend of fouling rate for central module; intermittent aeration with relaxation (at a SAD_m of 0.24 Nm^3 m^{-2} h^{-1})

8.3.2 Critical aeration demand

Two separate studies were conducted to determine $SAD_{m,crit}$ of the central module operating with intermittent and continuous aeration. The membrane was operated at a constant flux of 14.5 l m^{-2} h^{-1}, with cyclic permeation (15 min on/1 min relaxation) for both the studies. The aeration-step experiment was performed to determine $SAD_{m,crit}$ of the central module under conditions of intermittent aeration (10 sec on/10 sec off). A correlation of fouling rate with SAD_m between 0.03 and 0.3 Nm^3 m^{-2} h^{-1} (Figure 8.3) revealed a $SAD_{m,crit}$ of 0.19±0.01 Nm^3 m^{-2} h^{-1}. The second aeration-step experiment performed to determine $SAD_{m,crit}$ of the same central module with continuous aeration, stepping SAD_m from 0.06 to 0.6 Nm^3 m^{-2} h^{-1}, revealed $SAD_{m,crit}$ to be in the range 0.06±0.05 Nm^3 m^{-2} h^{-1} (Figure 8.3). The critical aeration studies thus

reveal $SAD_{m,crit}$ for intermittent aeration to be higher than that for continuous aeration $SAD_{m,crit}$, implying that the latter is more energetically efficient.

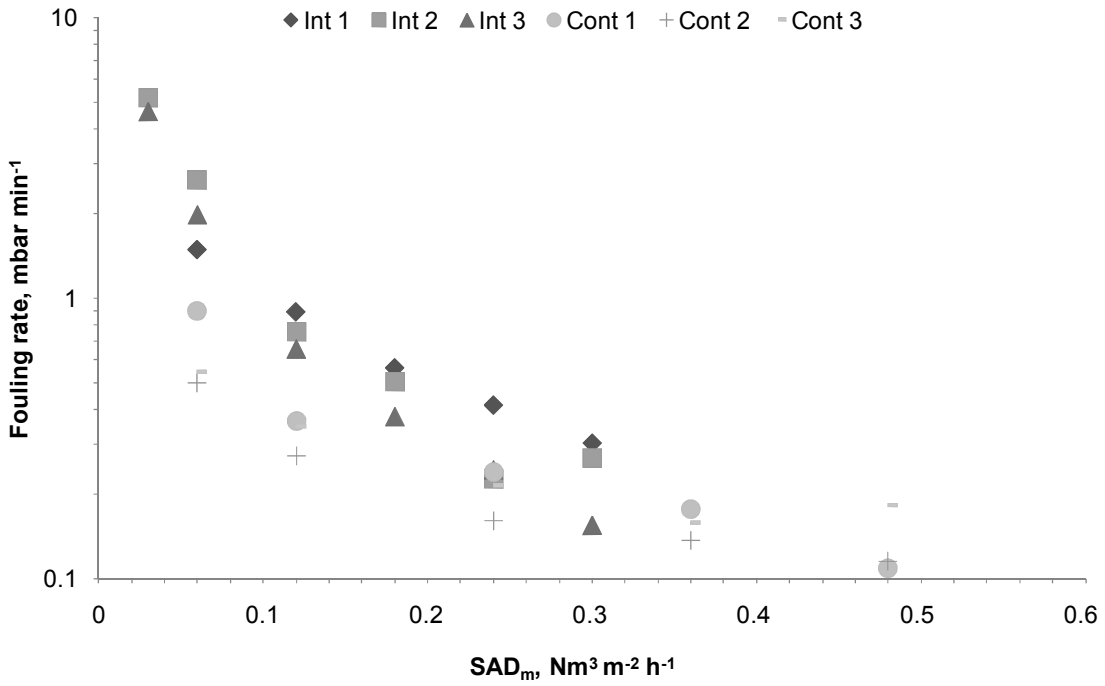

Figure 8.3 Comparison of effect of intermittent and continuous aeration regimes on fouling rate (constant flux of 14.5 l m^{-2} h^{-1})

8.4 Discussion

8.4.1 Effect of aeration on membrane permeability

Fouling control and flux enhancement of biomass filtration membranes using aeration has been extensively studied (Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007; Ueda *et al.*, 1997). Research reveals the effectiveness of aeration to depend on the design of the aerator (coarse/fine bubble) and module (HF or tubular membrane diameter, packing density, module spacing, *etc.*) (Chan *et al.*, 2007; Cui *et al.*, 2003).

The initial flux-step experiment performed to determine the critical flux of the individual modules revealed that whilst the exponential relationship between fouling rate and flux was similar for all three modules, the exponent value being around 0.1 for fouling rate expressed in mbar min^{-1} and flux in l m^{-2} h^{-1}, the permeability of the central module was higher than that of the outer modules. The presence of the membrane modules on either side of the central module meant that it channels were formed to direct the air bubbles past the membrane fibres and prevent their dissipation into the bulk liquor. It is well known that a channel or spacing within a immersed membrane module has an important effect on the hydraulic performance of the system (Cui *et al.*, 2003). Since modules in an MBR are predominantly in the centre of the stack, for example manufacturer data of the GE Zenon ZeeWeed® 500d module indicates that more than only 5% of all modules are at the outside of the stack, it is more reasonable to base studies on the central module than the external ones.

The flux-step experiments indicated J_c values to be somewhat lower than those reported for other pilot-scale studies on municipal feedwater (Table 8.3). In the past several different methods have been adopted to interpret J_c. Bouhabila *et al.* (1998), determined J_c from correlation of TMP with J and interpreted J_c as being the flux at which there is a sudden increase in TMP. This was refined by Le-Clech *et al.* (2003), and subsequently by Guglielmi *et al.* (2007), who defined J_c as the maximum flux at which the permeability (K) was greater than 90% of K_0, K_0 being the permeability measured at the first flux-step. More recently, Bottino *et al.* (2009) defined J_c as the J at which dTMP/dt≥0.5 mbar min^{-1}, a very simple definition based on practical considerations though insufficiently conservative given that it equates to a fouling rate of 0.72 bar a day.

8.4.2 Critical aeration rate

It has been recognised for some time that a threshold membrane aeration rate exists above which no further suppression of fouling takes place (Ueda *et al.*, 1997). This trend has since been corroborated by a number of authors (Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007; Bouhabila *et al.*, 1998) and formed the basis for empirically modelling aeration energy demand (Verrecht *et al.*, 2008). However, this key threshold value – denoted as the critical aeration demand $SAD_{m,crit}$ in this study – is evidently system dependent (Table 8.3), varying with the membrane module design and, presumably, the process operating conditions.

From the results it can be observed that for the same limiting fouling rate of 0.5 mbar min^{-1} the $SAD_{m,crit}$ (0.19±0.01 $Nm^3\ m^{-2}\ h^{-1}$) for intermittent aeration regime is lower than the aeration rate of 0.24 $Nm^3\ m^{-2}\ h^{-1}$ employed for the critical flux-step experiment. Similarly the $SAD_{m,crit}$ of 0.06±0.05 $Nm^3\ m^{-2}\ h^{-1}$ used for continuous aeration regime is much lower than the 0.24 $Nm^3\ m^{-2}\ h^{-1}$ aeration rate used for the critical flux-step experiment. The operating conditions identified on the basis of the critical flux-step experiment thus appear to be over conservative.

Table 8.3 Critical flux studies performed in real wastewater

System	Membrane configuration	Membrane area, m^2	J_c, $l\ m^{-2}\ h^{-1}$	J_c definition	MLSS, $g\ l^{-1}$	SAD_m, $Nm^3\ m^{-2}\ h^{-1}$	Reference
iMBR (LS)	HF	0.02	10.3 12.1 13.3	dTMP/dt ≥ 0.5	8	9	Bottino *et al.*, 2009
iMBR (PS)	HF	69.8	24.9-31	K > 90% K_0	10	0.3-1	Guglielmi *et al.*, 2007a
iMBR (PS)	FS	108	28	K > 90% K_0	7.7	0.35	Guglielmi *et al.*, 2007b
iMBR (PS)	FS	40	31.2	K > 90% K_0	20	0.88	Guglielmi *et al.*, 2008
iMBR (LS)	HF	0.016	25	Hydraulic tests (changes in TMP for different fluxes)	8.2	25	Bouhabila *et al.*, 1998
iMBR (PS)	HF	0.5	30		8.2	3.6	
iMBR (PS)	MT	0.19	15-19	Different criteria tested	8	0.87	Le Clech *et al.*, 2003
iMBR (PS)	HF	3.33	14.5	dTMP/dt ≥ 0.5	8	0.24	Current study

LS: Lab-scale; PS: Pilot-scale

Previous studies performed on GE Zenon HF membranes have assumed that intermittent aeration can be used to effectively control fouling and improve membrane permeability (Guglielmi *et al.*, 2007; Garcés *et al.*, 2007; DeCarolis Jr. and Adham, 2007; Fatone *et al.*, 2007). Pilot and full-scale trials have been recently conducted to determine the effect of decreased intermittent aeration on permeability (Garcés *et al.*, 2007; Tao *et al.*, 2009). Garcés *et al.* (2007) evaluated the impact of a 50% reduction in aeration rate through the established aeration regime of 10"/10" (10 s on, 10 s off) against two other aeration regimes of 10"/30" and 10"/10" with 50% less air. The results at low and medium fluxes (under 50 l m^{-2} h^{-1}) revealed that under either condition of 50% aeration, there was no significant difference in TMP behaviour when compared to the established aeration regime. This result indicates that reduced aeration through intermittent application is more efficient than continuous aeration, a result corroborated by the study of Tao *et al.* (2009), but contrary to the results from the current study. This may be a facet of the rather unusual sludge, which had a very high SVI and was not readily filterable, encountered in the current study.

8.5 Conclusions

A pilot-scale trial was conducted to assess the performance of a hollow fibre membrane. The outcomes from the J_c and $SAD_{m,crit}$ correlations are as follows:

- Initial flux-step trials on the three individual membranes revealed the permeability of the two outer membrane modules to be lower than that of the central module, indicating that tests are most representative if conducted on the central module rather than the three-module module.

- The J_c of the central module (14.5 l m^{-2} h^{-1}) was low in comparison to other pilot-scale trials of HF membranes operated under similar conditions and similarly challenged with municipal effluent.

- The aeration-step method revealed that for constant flux operation there was a $SAD_{m,crit}$ value below which a significant increase in membrane fouling arose, analogous to the critical flux trends. $SAD_{m,crit}$ can thus be used to optimise the aeration rate for immersed HF membrane systems.

- The $SAD_{m,crit}$ for both intermittent and continuous aeration regimes was lower than the aeration rate used to identify the critical flux through flux-step experiments. This implies that the operating conditions identified for critical flux-step experiment are conservative.

- The aeration-step trials under the two different aeration regimes revealed that for any given SAD_m, continuous aeration is more effective at controlling the fouling rate intermittent aeration, which is counter-intuitive and contrary to industrial practice. Further trials need to be carried out on full-scale installations to verify these counter-intuitive findings.

- The $SAD_{m,crit}$ value (0.19 Nm^3 m^{-2} h^{-1}) for the central module, is slightly less than the mean values of SAD_m (0.25 Nm^3 m^{-2} h^{-1}) recommended by the supplier, and also less than data reported for a number of full and pilot-scale applications (Verrecht *et al.*, 2008).

The results suggest that measurement of $SAD_{m,crit}$ by aeration stepping offers a more appropriate method for identifying the optimal operating conditions of an MBR, particularly for most full-scale plant where operation is invariably below the critical flux.

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9 CRITICALITY OF FLUX AND AERATION ON DIFFERENT HOLLOW FIBRE MEMBRANE BIOREACTOR AND SLUDGE QUALITY IMPACT

Ana Santos[1], Wenjing Ma[2], Irene Somoza[3], Hèctor Monclús [4], Peter Aerts[3] and Simon J. Judd[1]

[1]Centre for Water Science, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK
[2]Shenyang Research Institute of Chemical Industry, Shenyang, China
[3]Chemical Process Engineering Department, RWTH Aachen University, Aachen, Germany
[4]Faculty of Sciences, University of Girona, Girona, Spain
[5]Dow Water Solutions, Midland, MI, USA

Abstract

Critical flux measurement has been widely employed as a means of determining the optimum condition for operating membrane bioreactors. However, the technique is subject to limitations relating to the impact sudden changes in hydraulic loading have on the instantaneous rate of fouling, when the flux is instantaneously incrementally increased. The use of incremental stepping of aeration allows criticality to be identified under more benign conditions, but has not been extensively investigated. The critical flux and aeration of five different hollow fibre (HF) membrane modules have been measured when challenged with a municipal wastewater feed and the data compared.

The impact of CST, SMP and turbidity on membrane fouling were counter-intuitive, particularly at higher aeration rates. Although the data were significantly scattered, consistently higher critical fluxes were determined for fibres with higher permeability which were none-the-less somewhat lower than those reported in the literature.

9.1 Introduction

The advantages offered by membrane bioreactor (MBR) technology have been recognised for some time. These include higher quality effluent, smaller footprint when compared to classical biological treatment and the ability to operate with uncoupled hydraulic and solids retention times (HRT and SRT, respectively). However, the MBR technology is more costly, both in capital (capex) and operating (opex) costs, than the conventional ASP on which it is based (Verrecht *et al.*, 2008), mainly due to the constraints imposed by membrane fouling and clogging (Judd, 2008; Yigit *et al.*, 2009).

Key contributors to the opex of an immersed MBR (iMBR) are aeration and membrane replacement (Verrecht *et al.*, 2008; Yigit *et al.*, 2009; Kennedy and Churchouse, 2005; Verrecht *et al.*, 2010), of which aeration energy demand is normally the most significant. Aeration is required to maintain solids in suspension and provide the biomass with oxygen for the biotreatment component of the process, and scour the membrane surface to maintain its permeability. Previous studies at pilot plant scale have demonstrated that there is a linear relationship between flux and aeration rate up to a threshold value beyond which no further increase in permeability take place (Ueda *et al.*, 1997; Le Clech *et al.*, 2003; Guglielmi *et al.*, 2007). This affords the opportunity to reduce opex by lowering the flux, and thus the specific membrane aeration demand with respect to the membrane area (SAD_m). However, this is only achieved through increasing the capital cost by installing more membrane area.

Optimisation of MBR operation can proceed through the classical flux step analysis to identify the so-called critical flux (J_c), originally defined as the flux below which no deposition of foulants takes place (Field *et al.*, 1995) but is now more practically defined as the flux above which fouling becomes significant. The flux step method involves the incremental increasing of flux until the rate of increase in the transmembrane pressure (dTMP/dt) becomes significant. However, the absolute critical flux value obtained by this measurement is dependent not only on the system design and operation but also on exact

method employed for its determination, in particular, the rate at which the flux is varied with time (Le Clech *et al.*, 2003; Judd and Judd, 2006), since the sudden change in hydraulic loading at the start of each step tends to exacerbate fouling (Table 9.1).

More recently, the use of aeration stepping has been explored as a means of identifying the critical condition, either by reducing the bulk aeration rate (Chapter 8) or increasing its intermittency (Verrecht *et al.*, 2010). This provides more benign conditions for determining the critical condition (*i.e*. the maximum flux at the minimum aeration rate) since this changes the shear at the membrane:solution interface rather than the hydraulic loading. Initial reports have indicated that more optimum critical conditions are identified by this method (Chapter 8). In the current study, a more extensive range of hollow fibre (HF) membrane characteristics are investigates to attempt to establish any inter-relationship between the nature of criticality and HF membrane dimensions.

Table 9.1 Critical flux values reported for immersed system in pilot-scale treating real wastewater

System	Area, m^2	J_c, $l\ m^{-2}\ h^{-1}$	J_c definition	MLSS, $g\ l^{-1}$	SAD_m, $Nm^3\ m^{-2}\ h^{-1}$	Aeration regime	Reference
HF	208.8	15-45	Hydraulic tests (changes in TMP for different fluxes)	10-21	-	Intermittent: 10 sec on/10 sec off	Fan *et al.*, 2006
HF	69.8	24.9-31	$K > 90\% K_0$	10	0.3-1	Intermittent: 10 sec on/10 sec off	Guglielmi *et al.*, 2007
HF	0.5	30	Hydraulic tests (changes in TMP for different fluxes)	8.2	3.6	-	Bouhabila *et al.*, 1998
HF	60	30	Observation of TMP and flux behaviour	10-12	0.83	Intermittent: 10 sec on/10 sec off	Jiang *et al.*, 2005

(-) not specified

9.2 Materials and Methods

The MBR pilot plant installed at Cranfield University was operated intermittently for five campaigns between July 2008 until September 2010. During the five campaigns, the flux and aeration criticality of five immersed HF membrane modules and four sidestream HF membrane modules (Appendix C) were tested.

During Campaign 1 (Chapter 8), a three-module HF immersed cassette was tested (*S2*, Table 9.2). Results revealed that the tests would be more representative if conducted on the central module, and all tests subsequently performed on immersed modules were always carried out exclusively on the central module.

Three new immersed modules were tested during Campaign 2 (*B1*, *B2*, *S1*, Table 9.2), and of the four modules (*B1, B2, S1, S2)*, the one with highest permeability was selected for further tests (*S2*). Campaigns 3 and 4 were performed under similar experimental conditions of continuous and intermittent aeration at high and low MLSS, respectively to evaluate the impact of sludge characteristics on criticality determination. During this campaign, two sidestream HF modules were operated in parallel (Appendix C).

For the final campaign (Campaign 5), a new immersed module (*B3*) was tested in parallel with two more novel sidestream HF modules and the step tests performed under continuous and intermittent aeration for both flux and aeration criticality evaluation at high MLSS.

9.2.1 MBR pilot plant

The pilot-scale plant comprised a 2.5 m^3 bioreactor operating continuously with a immersed membrane module used to control the hydraulic and solids retention time (HRT and SRT, respectively) (Figure 9.1). For the test modules, a vertically-mounted cassette fitted with three membrane modules was installed (Figure 9.1; Table 9.2). The cassette was immersed to a depth of 0.5-1.0 m in the bioreactor and permeate was extracted using a peristaltic pump (Model 520 Du, Watson Marlow). The pressure change was continuously monitored using of pressure transducer, located in the permeate line, which was connected to a dedicated data logger (Pico data logging system, Pico Technology). Under the experimental conditions used, the pressure of the retentate was constant and the TMP assumed to vary only with changes in permeate pressure due to fouling. TMP was taken to equate to the difference between the mean hydraulic head at the mid-point of the membrane module and the permeate pressure.

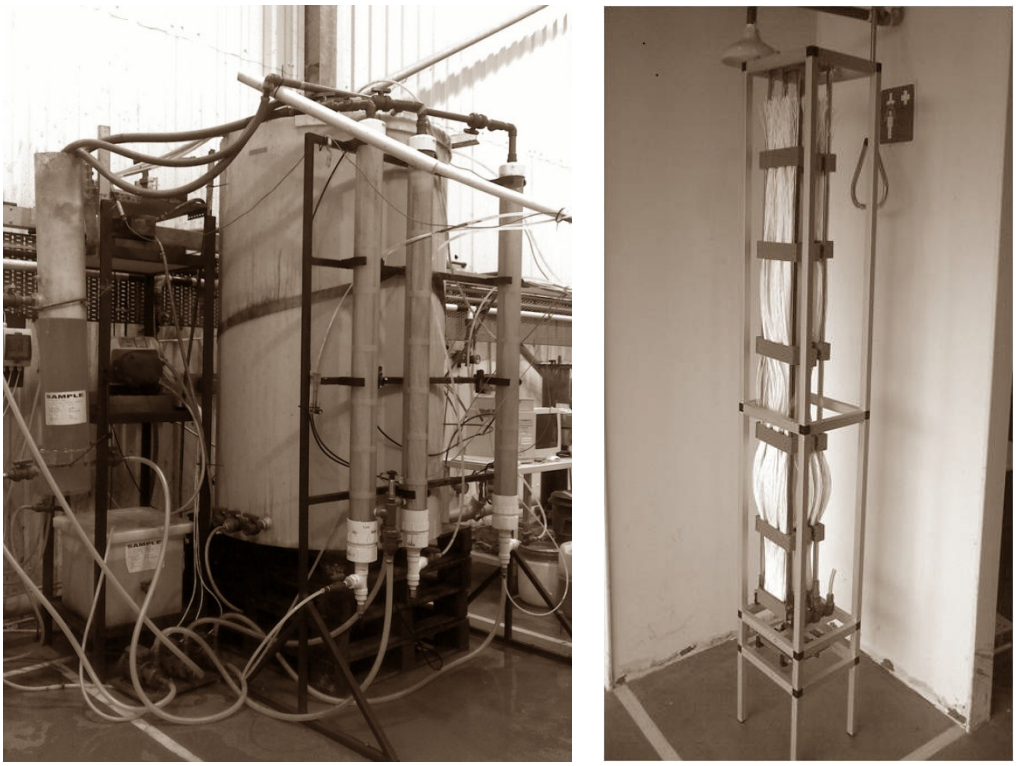

Figure 9.1 MBR pilot plant overview and membrane modules cassette

The plant was fed with settled sewage from the primary settlement tank at the Cranfield University WwTW. Throughout the campaigns removal of COD and ammonia was always greater than 80% with an average influent concentration of 285.2 (±99.6) for COD, 27.2 (±11.2) for NH_4, 2.52 (±3.32) for NO_3 with a pH of 7.4 (±0.32). Aeration of the biological process was regulated with a motorized-valve to keep the dissolved oxygen concentration around a set-point of 2 mg l^{-1}. The control module was operated at a mean permeate flux of 7.3 l m^{-2} h^{-1}, an average HRT of 19 h and with no sludge wasting. During Campaigns 2, 3, 4 and 5, the MLSS was held between 3 and 7 g l^{-1}.

Table 9.2 Modules characteristics for the five immersed membrane modules

	B1	*B2*	*B3*	*S1*	*S2*
Membrane material	Proprietary PVDF				
Preservative	Hydrophilic, no preservative				
Nominal pore size, µm	0.12		0.15	0.08	
Outer diameter, mm	2.45	2.35	2.2	1.3	1.4
Inner diameter, mm	1.2	1.2	1.2	0.9	0.9
Number of filaments	288	288	288	517	517
Pure water permeability, l h^{-1} m^{-2} bar^{-1}	280-300		913	350-400	
Filament length, mm	1500				
Module area, m^2	3.33				
Module number	3				
Cassette area, m^2	10				
Module size (L x W x H), mm	169 x 40 x 1620				
Cassette size (L x W x H), mm	400 x 300 x 2140				

9.2.2 Physico-chemical analyses

Biomass quality was monitored daily for mixed liquor (volatile) suspended solids (MLSS and MLVSS, respectively), sludge volume index (SVI) and capillary suction time (CST), determined according to the standard methods (APHA, 1998). Particle size was measured by laser diffraction (Mastersizer 2000, Malvern Instruments, UK). Biomass was centrifuged at 6,483 *g* for 20 minutes (Sorvall Legend RT+ centrifuge, Thermo Scientific, UK) and the clarified fraction assayed for soluble chemical oxygen demand (sCOD) and turbidity measurement according to standard methods (APHA, 1998). For the soluble microbial product (SMP) quantification, biomass was filtered through a 1.2 μm pore size glass microfibre filter (Munktell Filter AB, Sweden) and the filtrate analysed using a Shimadzu TOC-5000A analyser.

Water quality determinants monitored included chemical oxygen demand (COD), ammonia (NH_4^+-N) and nitrate (NO_3^--N), all according to the standard methods (APHA, 1999), with the influent and effluent sampled 2-3 times *per* week.

9.2.3 Critical flux and aeration

All criticality tests were performed on the central module of the cassette, this being the most representative of a full-scale cassette where modules are predominantly in the centre of the cassette (Chapter 8). The critical flux was assumed to be the flux at which the fouling rate, dTMP/dt, exceeded a threshold of 0.5 mbar min^{-1} (Chapter 8). The same criterion was applied to the critical aeration demand test. Each test was triplicated, under experimental conditions outlined in Table 9.3. From campaigns 3 to 5, the bioreactor aeration was switch off to avoid interference with the ongoing test.

Table 9.3 Experimental conditions for criticality test

Critical flux (J_c)	Value
Filtration flux, l m^{-2} h^{-1}	5-35 (intervals of ~5)
Filtration cycle	9 min on/1 min off (relaxation)
Filtration duration (total), min	20
SAD_m, Nm^3 h^{-1} m^{-2}	Continuous: 0.48[a]
	Intermittent: 0.24
Aeration frequency	Continuous
	Intermittent: 10 sec on/10 sec off
Critical aeration ($SAD_{m, crit}$)	
Filtration flux, l m^{-2} h^{-1}	Fixed at critical flux previously observed
Filtration cycle	14 min on/1 min off (relaxation)
Filtration duration, min	30
SAD_m, m^3 h^{-1} m^{-2}	Continuous: 0.6 to 0.06 (intervals of 0.12)
	Intermittent: 0.3 to 0.03 (intervals of 0.06)
Aeration frequency	Continuous
	Intermittent: 10 sec on/10 sec off

a: values typically recommend for immersed HF modules by manufacturers.

Prior to each test a chemically-enhanced backflush (CEB) was applied using a 500 mg l^{-1} sodium hypochlorite (NaOCl) solution, the cleaning protocol comprising 5 pulses at 55 l m^{-2} h^{-1} of 15 seconds each with 5 minutes relaxation between the pulses. Following a complete set of critical flux and aeration experiments an *ex-situ* clean was performed. The cassette was removed from the reactor and the three modules individually rinsed with water and left overnight in an aerated tank with water containing 0.1% NaOCl solution. When not in use the modules were stored in a 0.1% NaOCl solution.

9.3 Results

9.3.1 Criticality tests

To assess the criticality of flux and aeration demand, flux and aeration were stepped according to the experimental condition outlined in Table 9.3. The intermittent regime and the experimental condition used for this campaign followed those reported earlier (Chapter 8). During Campaign 2, the flux step data for the four modules tested (Figure 9.2) indicate the smaller diameter fibres (*S1* and *S2*) to have higher permeability and lower fouling rates than the larger-diameter fibres under conditions of high flux. Under intermittent aeration conditions, the critical flux was estimated to be 9.0 and 6.9 l m^{-2} h^{-1} for *B1* and *B2* respectively, compared with and 8.4 and 13.0 l m^{-2} h^{-1} for *S1* and *S2*, respectively, slightly higher (14.5 l m^{-2} h^{-1}) than reported by Monclùs *et al.* (2010) (Chapter 8). Of the modules tested, *S2* and *B2* provided the lowest and highest fouling rates respectively.

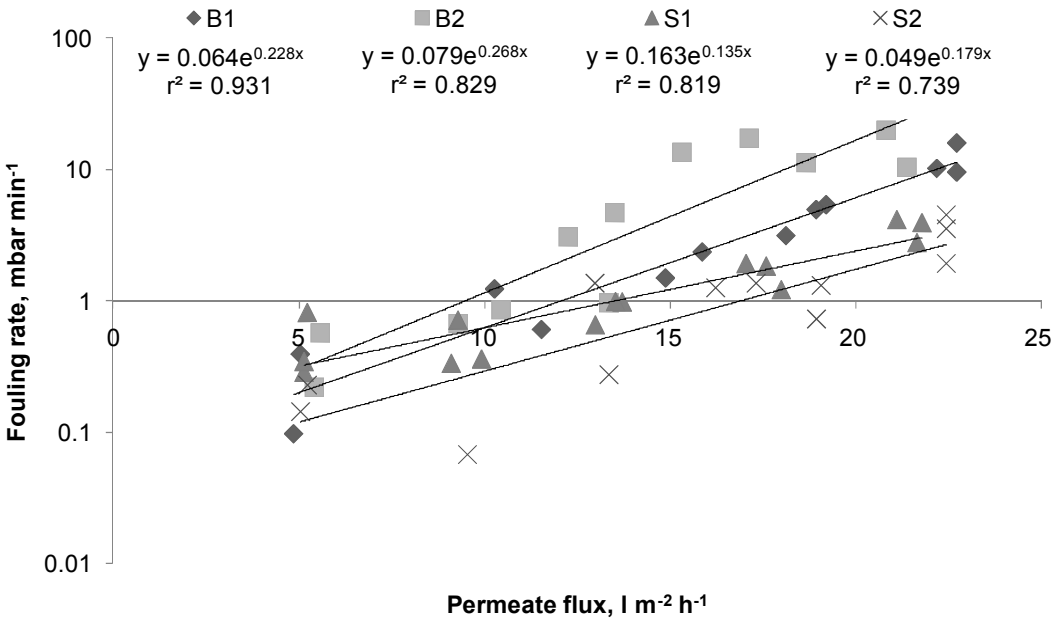

Figure 9.2 Fouling rate *vs* permeate flux for immersed modules, intermittent aeration

Aeration step trials conducted at the critical flux value identified from the previous tests reveal broadly similar trends for the *B1*, *B2* and *S2* fibres, with the lowest fouling rate of 0.5 mbar min^{-1} recorded under low air scouring conditions demonstrated by the *S1* fibre (Figure 9.3). This indicates that either the value of SAD_m used to determine the critical flux was conservative or, more likely, that the measured critical flux value was low. For the same threshold fouling rate of 0.5 mbar min^{-1}, the $SAD_{m,crit}$ for the modules *B1* and *B2* was, at 0.25 Nm^3 m^{-2} h^{-1}, similar to the SAD_m applied for the critical flux determination (0.24 Nm^3 $m^{-2}h^{-1}$), whereas for the *S2* module $SAD_{m,crit}$ was lower at 0.19 Nm^3 m^{-2} h^{-1}, comparable to the value reported by Monclùs *et al.* (2010) for the same fibre (Chapter 8).

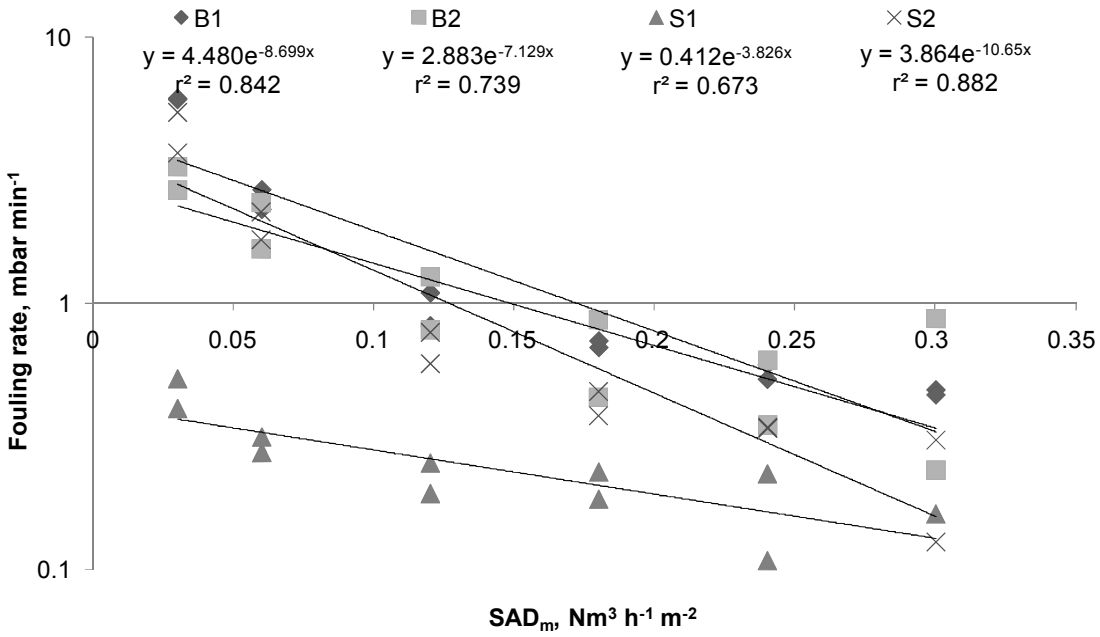

Figure 9.3 Fouling rate vs SAD_m for immersed modules at intermittent aeration

During Campaign 3, the *S2* module was tested under the same experimental conditions with the MLSS held at 6.5 g l^{-1} but with continuous aeration, reaching a critical flux of 11.9 l m^{-2} h^{-1} (Figure 9.4). The critical SAD_m value obtained was 0.99 m^3 h^{-1} m^{-2} (Figure 9.5; Table 9.4) higher than value obtain by Monclùs *et al.*, (2010) (Chapter 8) under the same aeration regime (Table 9.5).

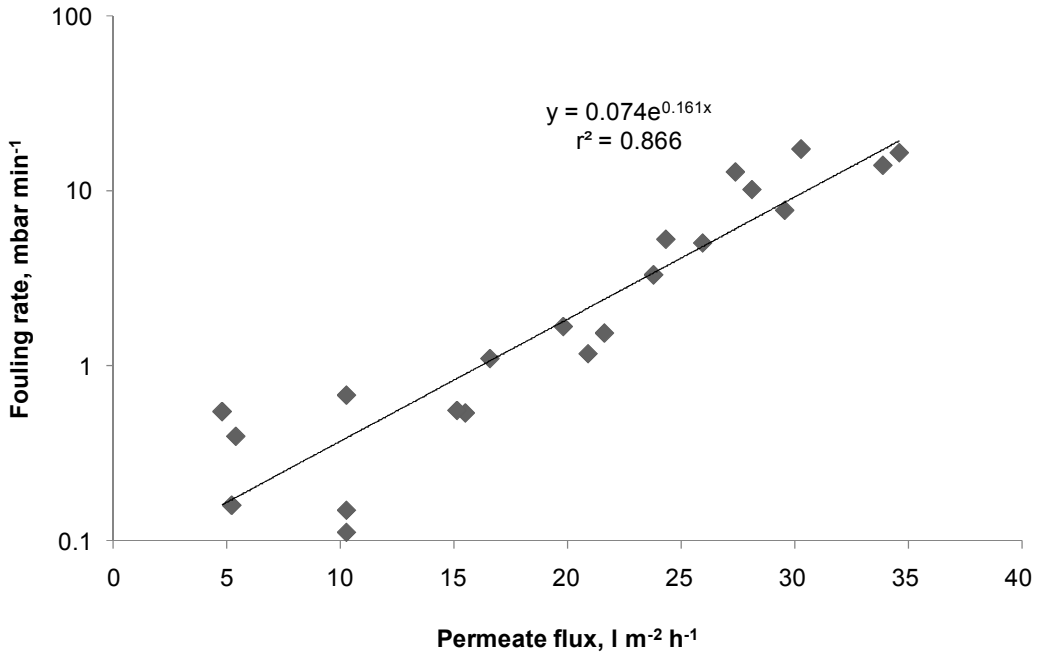

Figure 9.4 Fouling rate *vs* permeate flux for *S2* immersed modules at continuous aeration

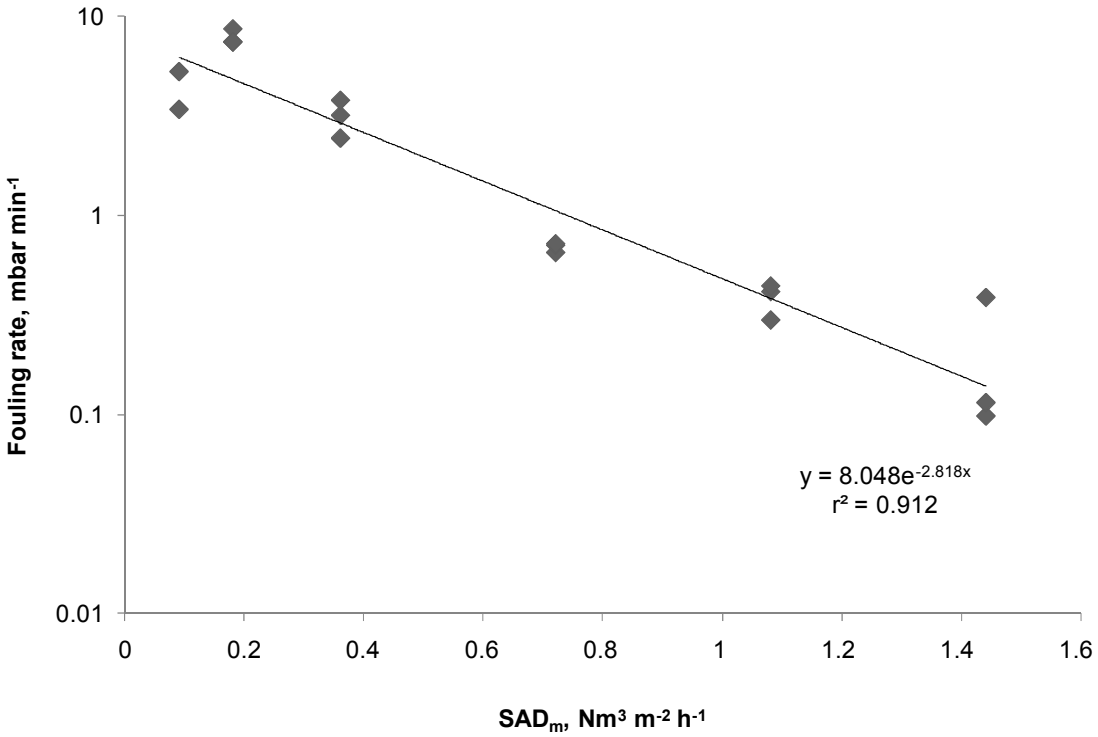

Figure 9.5 Fouling rate *vs* SAD_m for *S2* immersed modules at continuous aeration

During Campaign 4, the MLSS concentration was brought down to 3.3 g l^{-1} and the *S2* module tested under the same experimental conditions (Table 9.3) but with both continuous and intermittent aeration (Figure 9.6). For intermittent aeration, the critical flux determined was 12.4 l m^{-2} h^{-1} – lower than the value observed during Campaigns 1 and 2 but not considerably so. Under continuous aeration conditions, the critical flux was 13.0 l m^{-2} h^{-1} – somewhat higher than the value observed for the previous campaign.

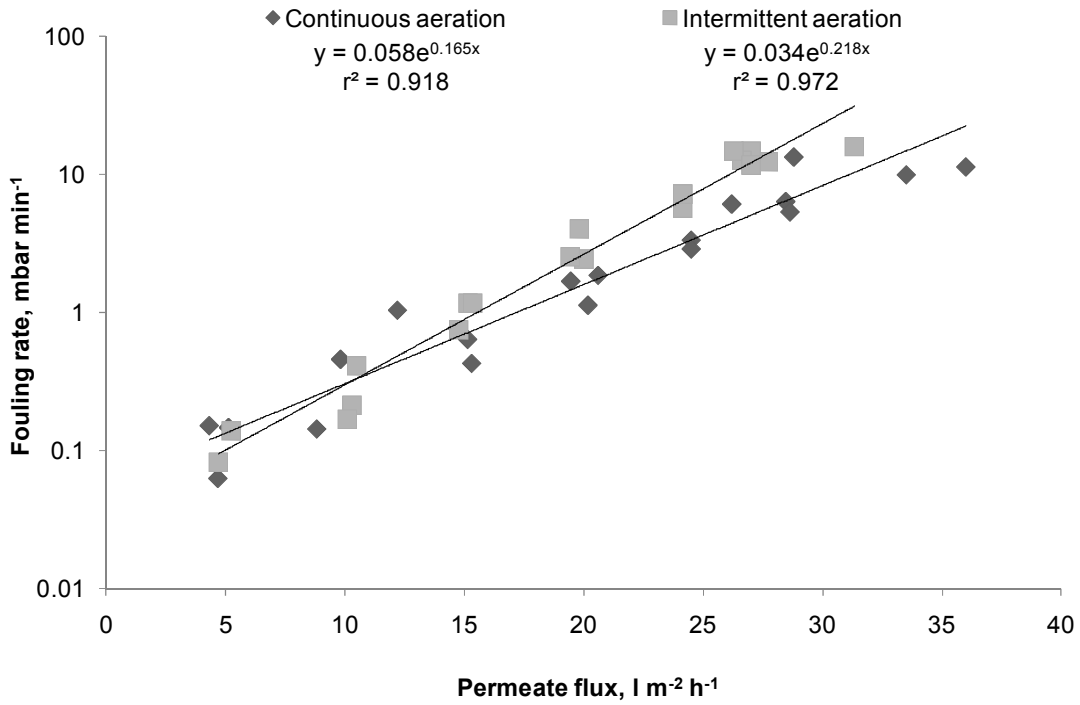

Figure 9.6 Fouling rate *vs* permeate flux for *S2* immersed module at continuous and intermittent aeration

The SAD_m tests performed at the measured critical flux revealed a critical SAD_m value of 0.62 and 0.39 $m^3\ h^{-1}\ m^{-2}$ under continuous and intermittent aeration, respectively (Figure 9.7).

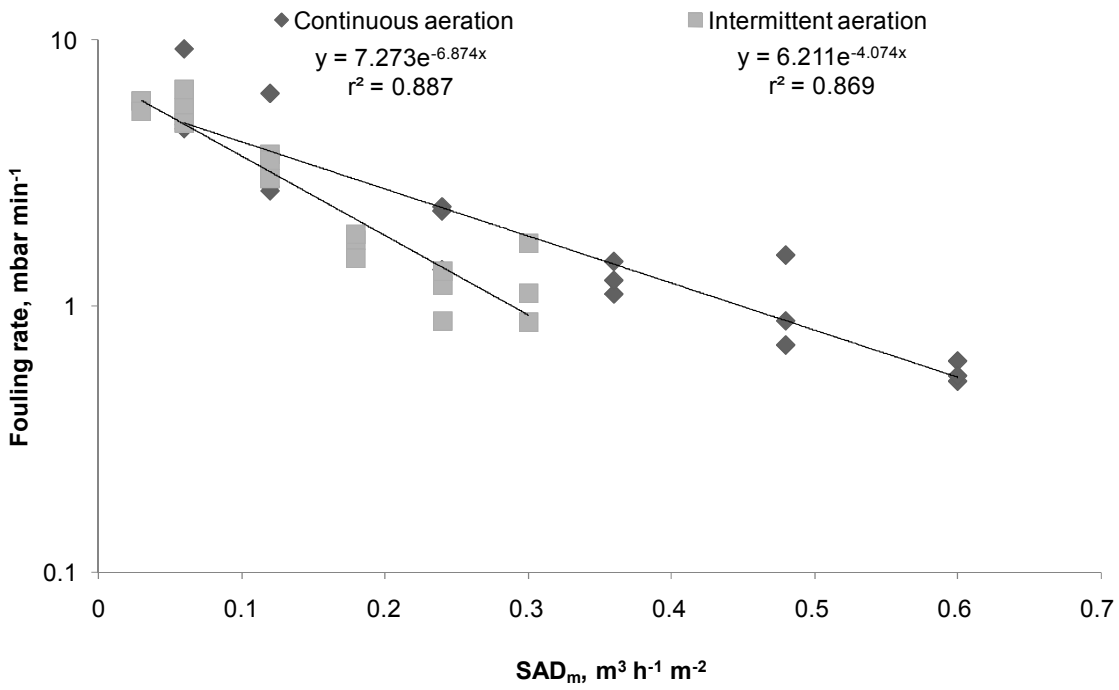

Figure 9.7 Fouling rate *vs* SAD_m for *S2* immersed module at continuous and intermittent aeration

During the last campaign, a new immersed HF module (*B3)* was tested at an MLSS concentration of 6.9 g l^{-1}. The flux step test (Figure 9.8) revealed a critical flux of 14.3 l m^{-2} h^{-1} under intermittent aeration conditions, higher than the values observed in the previous campaign. A higher critical flux of 17.0 l m^{-2} h^{-1} was recorded for continuous aeration. The SAD_m step tests performed at the measured critical flux (Figure 9.9) revealed a critical SAD_m of 0.35 and 0.59 m^3 h^{-1} m^{-2} under intermittent and continuous aeration conditions respectively, higher than the values observed in previous campaign (Table 9.4).

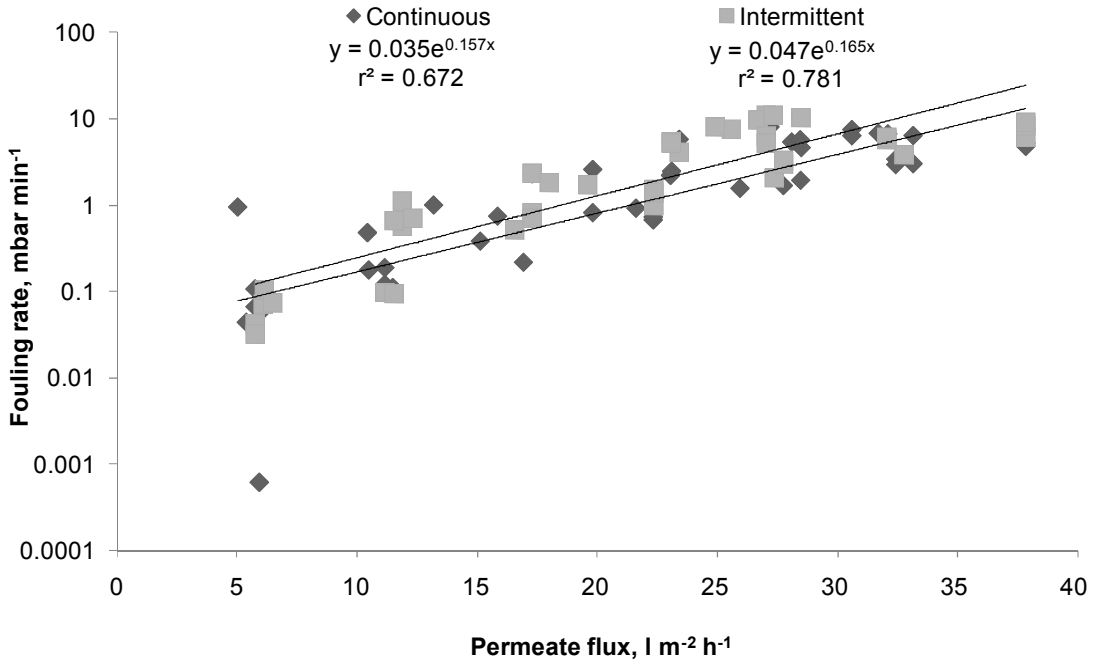

Figure 9.8 Fouling rate *vs* permeate flux for *B3* immersed module at continuous and intermittent aeration

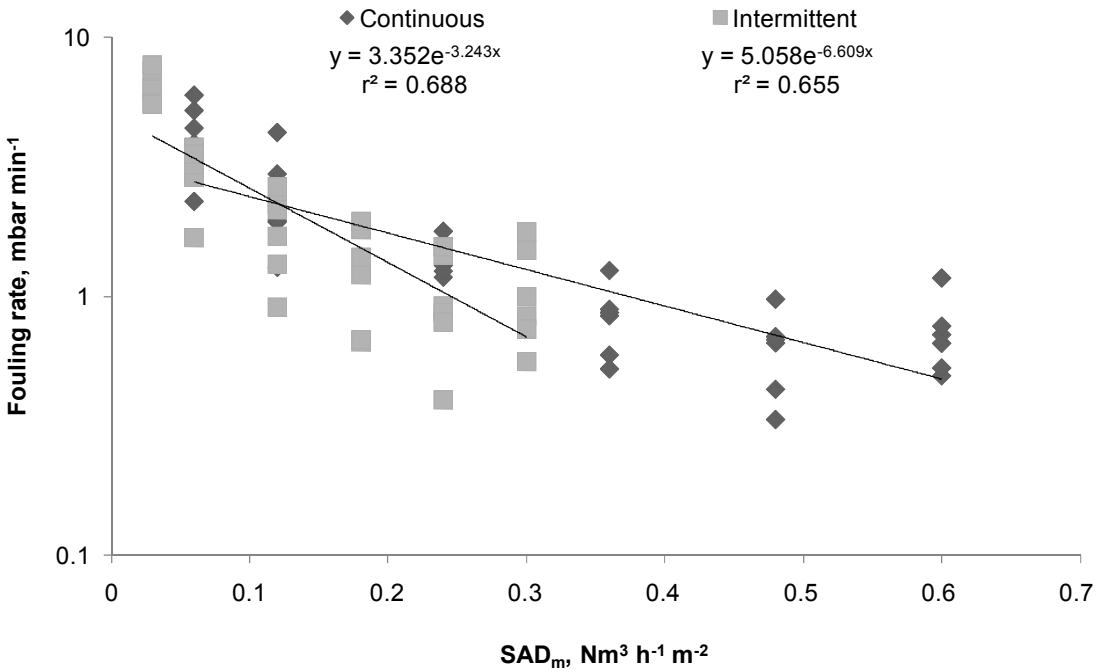

Figure 9.9 Fouling rate *vs* SAD_m for *B3* immersed module at continuous and intermittent aeration

For Campaigns 3-5, the aeration demand doubled, possibly due to the fact that the bioreactor aeration was switch off during the test performance. Also, assuming that at lower MLSS the fouling propensity increases (Rosenberger *et al.*, 2005), it would then be expected for increased aeration to be required to scour the membrane.

Table 9.4 Criticality of flux and aeration: summary table

Campaign	1*	2	3	4	5
Modules tested	*S2*	*S1, S2, B1, B3*	*S2*	*S2*	*B3*
J_c, l m^{-2} h^{-1}					
Continuous	-	-	11.9	13.0	17.0
Intermittent	14.5	8.4; 13.0; 9.0; 6.9	-	12.4	14.3
$SAD_{m, crit}$,Nm^3 h^{-1} m^{-2}					
Continuous	0.06	-	0.99	0.62	0.59
Intermittent	0.19	-0.05; 0.19; 0.25; 0.25	-	0.39	0.35

* See chapter 8; (-): no test performed

When analysing the r^2 correlation values some ambiguity on the obtained data is revealed. Given that the same experimental methodology for acquiring the data has been applied to each module, the poor replication of the data has been attributed to one or more of the following:

1. Data recording/monitoring issues
2. Differences in air scour, or some other mechanical operation and maintenance factor
3. Differences in module construction impacting on hydrodynamics
4. Differences in sludge fouling propensity, or some other physicochemical/biochemical factor

For the immersed modules, the signal is far less noisy when compared to sidestream module (Figure 9.10; Appendix C, Figure Appendix C.5 to Figure Appendix C.8) such that (1) is unlikely to be a significant contributor to irreproducibility. However, given the poor replication of the critical flux values between different modules built of the same material (*S1 vs S2*; *B1 vs B2*), it is clear that differences in fouling behaviour observed cannot be attributed entirely to changes in sludge quality.

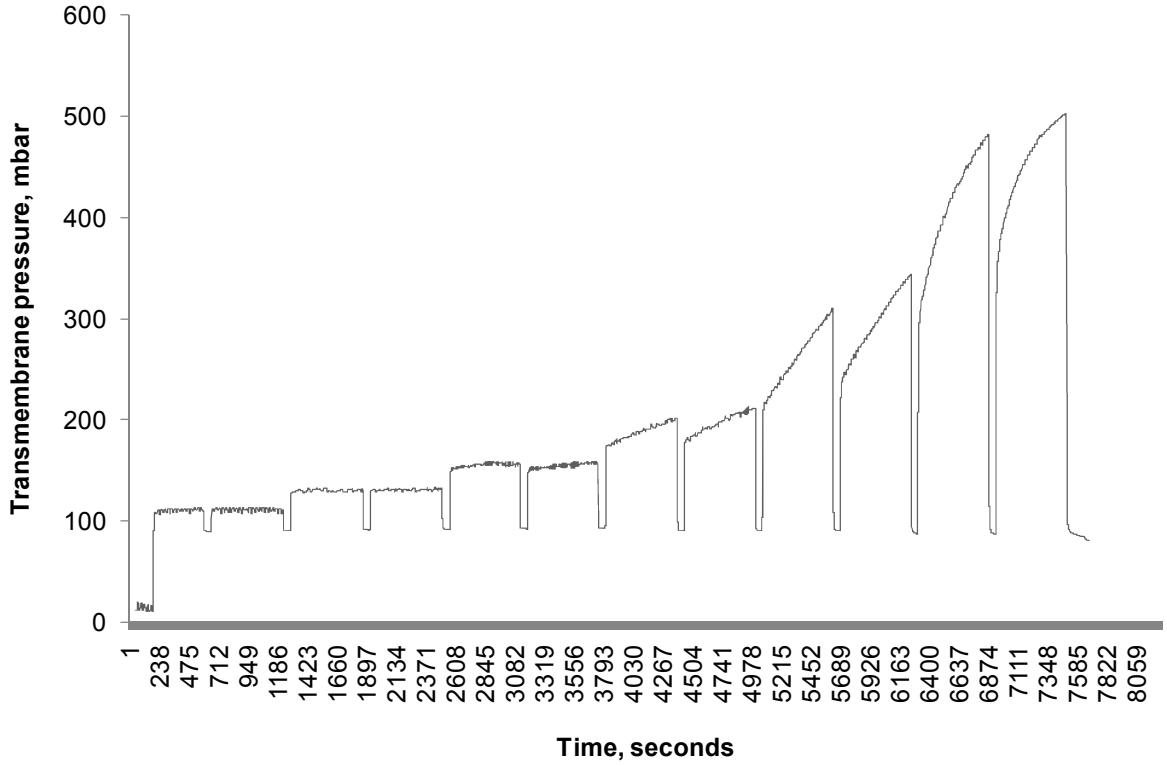

Figure 9.10 Transmembrane pressure *vs* time for an immersed module

Air scour (2) is unlikely to vary given that the aerator and modules are both fixed in the frame. Similarly, it is assumed that the modules are likely to have been replicated in their construction.

The most plausible explanation for the observed behaviour is the heterogeneous distribution of the permeate flow across the fibre bundles. This would normally be caused by the exclusion of large areas of the fibre.

Such exclusion in a full-scale MBR would be associated with clogging, but there was no indication of this throughout the trials. On the other hand, the nature of the fibre – specifically the sealing to the fibre tips (3) – means that it is susceptible to air locks: air precipitating on the permeate side of the fibre cannot readily escape from it through the top permeate header. Air collecting within the fibre would be expected to suppress permeation through creating a back pressure. It would also be expected to do this in a higher vagarious and unpredictable manner since the amount of trapped air would be expected to change temporarily and with operating conditions (and specifically the TMP).

From the critical flux values estimated according to the method summarised in Table 9.3, three key research questions arise:

a) Whether differences in the critical flux data are statiscally significant, given the degree of data scatter (Appendix D),

b) Whether the sludge fouling propensity changed significantly over the course of the study, and

c) Whether the fouling propensity is significantly higher than that reported in published studies

As sludge characteristics (4) are known have great impact on membrane fouling and so an examination of sludge fouling propensity is required.

9.3.2 Sludge fouling propensity

Fouling of MBR membranes by sludge is a widely explored phenomenon with three benchmark reviews produced within the last eight years (Drews, 2010; Le-Clech *et al.*, 2006; Meng *et al.*, 2009). However, despite the attention the subject has attracted, there is no accepted *ex situ* measure of sludge fouling propensity and no consistently identified membrane foulant derived from the sludge. It is generally accepted that soluble microbial product (SMP – in essence the organic carbon fraction of the clarified biomass) is the most representative measure of sludge fouling propensity, but even this is subject to debate. Three convenient sludge fouling determinants were used in this study were capillary suction time (CST), SMP and supernatant turbidity.

Innate fluctuations in feedwater quality produced correspondingly broad changes in sludge quality (Table 9.5) are unsurprising. However, on examination of the data for both sludge foulant determinants and critical flux (Figure 9.11), no pattern is evident.

The sludge for the *B2* fibre appears to have an exceptionally high fouling propensity, with the sludge CST and SMP 3-4 times higher than those recorded for the *S1*, *B1* and *B3* modules, and the critical flux was correspondingly lower. However, the fouling parameters for the *S1*, *B1* and *B3* trials indicated sludge of very similar quality but with a significantly higher critical flux recorded for the latter. This corroborates the data in Table 9.5, confirming that the higher critical flux recorded for *B3* reflects a greater fouling resistance (or higher sustainable flux) than the other fibres. On the other hand, the *S2* fibre was apparently challenged with sludge of higher fouling propensity – double the CST – and yet yielded only a slightly lower critical flux than *B3* and a considerably higher critical flux than *S1*.

Table 9.5 Sludge characteristics for campaign 2 to 5 (average±SD)

Campaign	2	3	4	5
MLSS, g l^{-1}	8.5 (±1.3)	6.5 (±0.2)	3.3 (±0.3)	6.9 (±0.5)
CST, seconds	72.0 (±53.6)	42.7 (±8.8)	19.8 (±4.2)	24.3 (±9.7)
SMP, mg l^{-1}	54.5 (±32.8)	43.0 (±6.4)	24.8 (±6.4)	25.6 (±8.2)

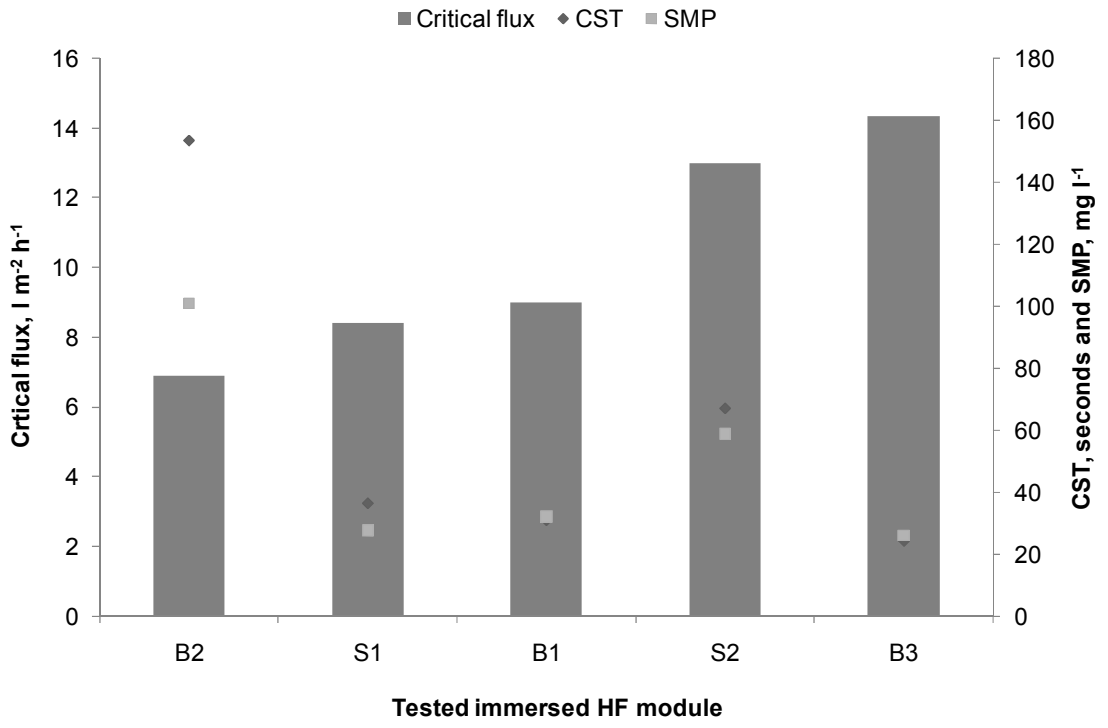

Figure 9.11 Sludge foulant determinants and critical flux data for campaign 2 and 5

Indeed, for the CST, SMP and the supernatant turbidity the trend in fouling is actually counter-intuitive, with fouling decreasing with increasing CST and SMP (Table 9.6). However, literature remains inconsistent and often contradictory and so the parameter responsible for membrane fouling is still unclear.

Table 9.6 Critical flux values reported for immersed system in pilot-scale treating real wastewater

System	J_c, l m^{-2} h^{-1}	MLSS, g l^{-1}	$SAD_{m,}$ Nm^3 m^{-2} h^{-1}	Sludge foulant determinant	Observation	Reference
FS	~8-70	1.6-2.4	1.9	SMP~25-120 mg l^{-1}	J_c ↓, ↑ SMP	Menniti and Morgenroth, 2010
HF	~15-45	10-21	15-45	SMP~4.2-52.1 mg l^{-1}	J_c ↓, ↑ SMP	Fan *et al.*, 2006
FS	~7-70	4.6-22	1-2.1	CST~5-50 seconds	J_c ↓, ↑ CST	Wang *et al.*, 2006

Two distinct regions can be observed (from Figure 9.12 to Figure 9.14): a region of low fouling, between SAD_m values from 0.24 to 0.48 m^3 m^{-2} h^{-1}, and a region of more severe fouling at an aeration intensity of 0.12 m^3 m^{-2} h^{-1}. Aeration has been shown to mitigate fouling, albeit with a threshold value beyond which the increase in air scouring no longer provides further benefits to fouling control being even deleterious for the sludge quality (Ueda *et al.*, 1997; Le Clech *et al.*, 2003; Wu *et al.*, 2008; Tacke *et al.*, 2008). At higher aeration intensities, the shear stress imposed on the biomass flocs may lead to an increase in the release of SMP by eroding EPS into solution (Ji and Zhou, 2006; Kim *et al.*, 2001; Wisniewski and Grasmick, 1998). Therefore, it is expected for the SMP, and so supernatant turbidity and/or DOC, to increase. However, although this was observed, the trend in fouling rate is actually counter-intuitive, with fouling decreasing with increased CST, SMP and supernatant turbidity.

Several authors have reported contradictory results about the influence of the MLSS on the critical flux (Le Clech *et al.*, 2003; Madaeni *et al.*, 1999; Rosenberger and Kraume, 2002). MLSS concentration in itself does not provide an indication of filterability, possibly due to significant unattributable changes in sludge rheology and thus hydrodynamics (Drews, 2010). For the concentrations ranges under study, the MLSS appears to have had a positive impact, decreasing fouling rate with increasing concentration.

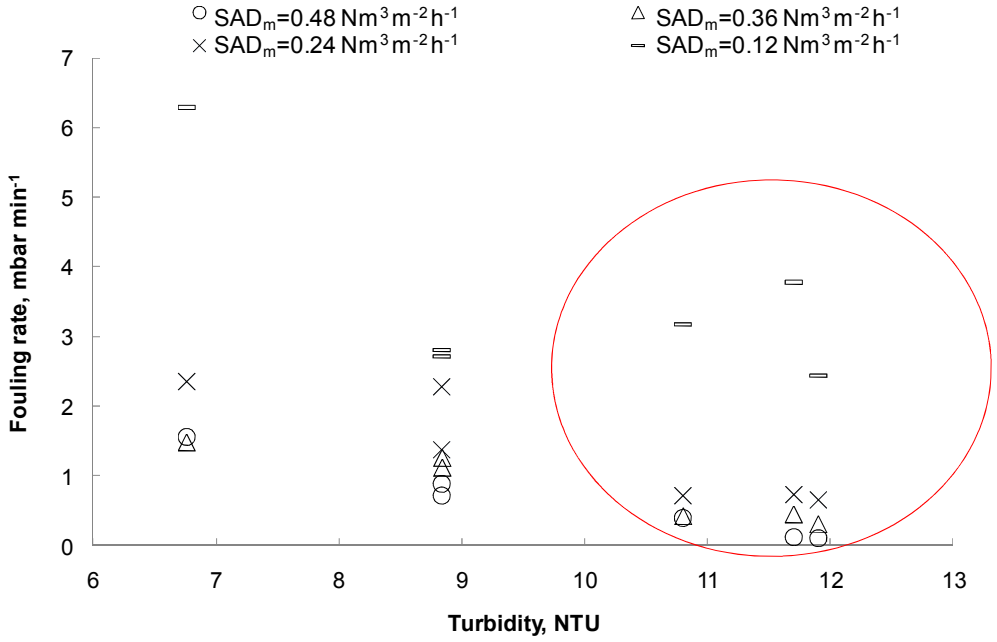

Figure 9.12 Fouling rate *vs* supernatant turbidity for *S2* immersed module at continuous aeration during campaign 3 and 4, with the encircled data referring to higher MLSS

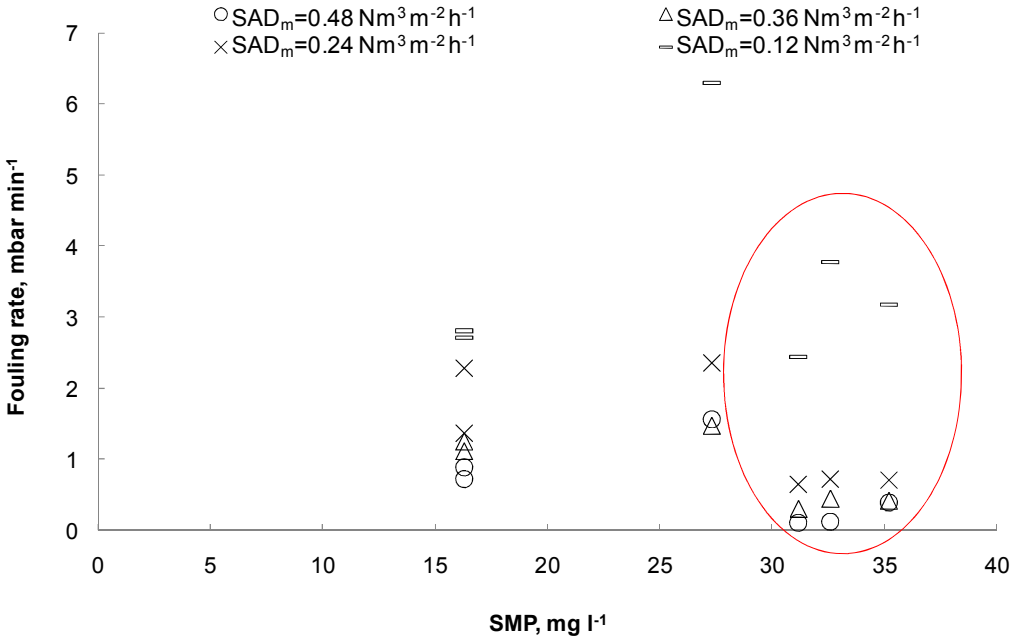

Figure 9.13 Fouling rate *vs* SMP for *S2* immersed module at continuous aeration during campaign 3 and 4, with the encircled data referring to higher MLSS

Further counter-intuitive results were obtained with CST. Whilst sludge filterability decreases with increasing CST, and thus increased fouling expected (Pan *et al.*, 2010), results show (Figure 9.14) lower fouling propensity at higher CST values, contrary to the findings of Wang *et al.*, (2006) who reported a 90% decline in critical flux estimated with increasing CST.

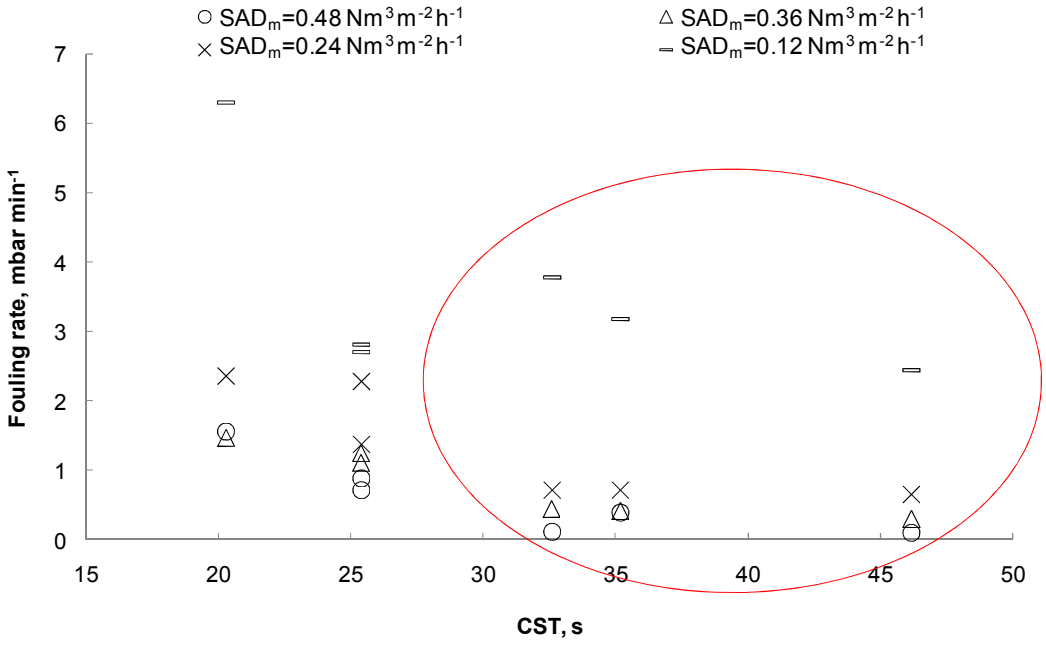

Figure 9.14 Fouling rate *vs* CST for *S2* immersed module at continuous aeration during campaign 3 and 4, with the encircled data referring to higher MLSS

9.4 Conclusions

- Tests have revealed consistently low fibre permeabilities. Whereas critical fluxes above 25 l m^{-2} h^{-1} have been routinely reported in similar pilot trials (Table 9.1), values below 15 l m^{-2} h^{-1} have been recorded throughout the current trials (Table 9.4). Whilst this may reflect more highly fouling conditions in these trials, published data for CST and SMP for some of these trials do not suggest a significant difference in sludge quality. Fan *et al.*, (2006), for example, reported SMP levels between 4.2 and 50 mg l^{-1} (*cf.* 20-60 mg l^{-1} for the current study) and attained critical fluxes as high as 70 l m^{-2} h^{-1}. In most cases, increasing SAD_m has been shown to make critical fluxes above 20 l m^{-2} h^{-1} attainable. This has not been the case in the current study.

- The difference between critical flux data from modules constructed of the same HF membrane is significant:

    - 9.0 *vs* 6.9 l m^{-2} h^{-1} for *B1* and *B2*
    - 13.0 *vs* 8.4 l m^{-2} h^{-1} for *S1* and *S2*

The module with highest recorded permeability was *B3*, with critical fluxes between 14 and 17 l m^{-2} h^{-1}. This is assumed to be due to *B3* fibres innately higher pure water permeability able to provide slightly higher sustainable fluxes.

- Although Monclùs *et al.*, (2010) (Chapter 8) observed lower critical SAD_m under continuous aeration, the aeration steps during Campaign 4 and 5 showed intermittent aeration to be more effective at controlling fouling than continuous aeration, which is beneficial in terms of energy savings and in keeping with industrial practice. However, when comparing the data obtain for the *S2* module (Campaign 1 and 4), there is an increase of 50 to 90% in aeration demand. This is likely to due to changes in the methodology employed.

- The modules with smaller fibres (*S1* and *S2*) showed lower fouling rates and better filtration performance than the larger-diameter fibre modules

(*B1* and *B2*) in all experiments performed. A smaller diameter is associated with greater fibre flexibility, which permits increased fibre movement from air scouring and so more shear and more effective fouling suppression.

- The difference between the critical flux indentified for the *B3* module and that of other modules equates to between 5 and 15% for intermittent aeration and 23-31% higher for continuous aeration when compared with *S2*. The corresponding values for the absolute difference in flux are 0.7-1.9 and 3.2-4 l m^{-2} h^{-1} respectively.

- The *B3* module operated under a biomass with good filterability characteristics partially explain its better performance. On the other hand, the *B2* module was challenged with the poorest quality sludge in terms of CST and SMP and yielded the lowest permeability. Whilst the low permeability can be explained by the poor sludge quality for *B2* module, the same is not true of the *S2* module which was operated under supposedly the second-most challenging filtration conditions of CST and SMP concentration whilst none-the-less providing the seconds highest permeability.

- Sludge fouling propensity measurement is hugely challenging, since there is no acknowledged convenient method of accurately testing it (and it is this which necessitates trials with real sewage). Three key parameters used to provide an indication of sludge fouling, CST, SMP and supernatant turbidity, have not been shown to correlate well with the fouling rate. Indeed, for both the CST and the supernatant turbidity the trend in fouling is actually counter-intuitive, with fouling decreasing with increasing CST. Similar vagarious trends have been reported in the literature and absolute values of more widely reported sludge foulants determinants do not differ significantly for those recorded in the current study. As for the MLSS concentration, there is no evident effect on membrane fouling.

9.5 References

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10 CONCLUSION AND FUTURE WORK

10.1 Conclusions

Metals form a key group of micropollutants and are subject to environmental legislation limiting their concentration in discharged effluents. An analysis of their comparative removal by membrane bioreactors (MBR) and conventional activated sludge process in municipal wastewater reveals:

- Whilst the benefits offered by membrane bioreactors (MBRs) with respect to permeate quality are generally recognised for determinants such as ammonia, microorganisms and suspended solids (Chapter 1), in the case of metals reported data indicates removal to be not significantly greater than that of the classical process. On average, MBR permeate contains about half the concentration of metals as effluent from the conventional activated sludge process (ASP). Although small differences were observed in the order of removal for ASPs and MBRs, no clear conclusions can be made given the scatter in the data. No clear trend was found in removal with increasing influent concentration either for ASPs or MBRs (Chapter 2).

- The dynamic and erratic nature of wastewater quality makes definition of metals speciation challenging, since it changes with pH, associated organic matter, and oxidation state. Operational parameters, and SRT in particular, may impact on metals removal through mixed liquor suspended solids (MLSS), colloidal and dissolved organic matter concentration. Feedwater quality may similarly influence metals removal. Metals removal appears to relate to the degree of complexation with organic matter, and specifically ligands which associate with the metal. The stability of the complexes formed is then determined by equilibrium thermodynamics, and specifically the stability constant K. However, it appears that complexation may either promote removal, if the organic is associated with the cell wall thus the solid phase, or diminish it, if

dissolved. The K values thus do not provide a reasonable indication of removal, an in any case vary with the chemical nature of the ligand (Chapter 6).

- Given the above, during biological treatment metals may either be associated with solids, and thus be removed through phase separation, or, if in dissolved form, through adsorption of complexes with organic ligands. The organic ligand concentration in the final effluent may relate to the dissolved BOD and COD, and colloidal organics may also be expected to contain metals. At higher SRTs and with improved removal of suspended solids, lower effluent COD and BOD concentrations result and this would be expected to coincide with reduced metals concentrations. This appears to be the case for Cu and Zn. However, whilst some authors report a significant increase in removal with SRT, it is generally small and varies between studies. On the other hand, some authors have claimed HRT to have a significant impact on removal for conventional ASPs indicating that there may be a kinetic element to metal retention. Levels of soluble metals tend to increase across the bioreactor, with the solubilisation of Zn being more pronounced than that of Cu at the highest SRT. In this case, it may be that more organic ligands are produce at higher SRTs, thereby promoting metal solubilisation (Chapter 5).

- Treating the return liquors stream, which is high in suspended solids concentration and would therefore be expected to increase the available binding sites for metals, leads to only a moderate increase in the removal of Cu and Zn (Chapter 5).

- The use of membranes in place of secondary sedimentation, although enhancing effluent quality in terms of suspended solids removal (less than 1 mg l^{-1}), provided no significant benefit in overall metal removal (Chapter 5). Given the ability to operate at higher SRT, metals removal would be expected to be enhanced in an MBR system through a higher solids surface area for metals adsorption. However, at the higher SRTs at which MBRs normally operate, there is apparently an increased concentration of dissolved organic matter promoting metals solubilisation, retaining them in solution and thus preventing their removal (Chapter 2). Bench-scale adsorption isotherm trials revealed that MBR has a lower specific adsorption capacity when compared to a conventional ASP (Appendix A). Given this and the high costs associated with this technology, both with respect to capital (capex) and operating (opex) costs, it is questionable that this technology provides sufficient additional benefit for it to be selected for metals removal.

- Given the variability in both metals concentration in wastewater and their removal by biological treatment, apparently as a result of their highly labile nature, it is questionable that the low EQS levels set by legislation can be considered realistic.

A study of a key organic micropollutant, permethrin, has revealed:

- The hydrophobic nature of micropollutants such as permethrin and PCP means that they are removed by adsorption onto solids, and so would be expected to be removed more readily at higher MLSS concentrations. Although there is a paucity of information with regards to permethrin, compounds with similar properties have been shown to be removed to a similar extent (Chapter 7).

- The acclimatisation period appears to have a significant impact on micropollutants removal; an increase on soluble COD was observed with reduced acclimatisation period employed. Effluent soluble COD concentration appears to provide a better indication of the residual permethrin concentration than the suspended solids, despite the expectancy of permethrin being associated with solids. A more comprehensive study is required to understand permethrin fate and behaviour during conventional wastewater treatment (Chapter 7).

MBRs are recognised as being an enhanced wastewater treatment technology whose implementation worldwide is rapidly increasing. A study of the last 20 years of research, commercialisation and implementation reveals:

- Of the commercially available immersed MBR products identified, the HF configuration leads the market with a wider diversity of material types and membrane module size than other configurations. PVDF and PES are the predominantly used materials, since these provide the desired pore structure and chemical resistance. PVDF materials are available across the entire range of pore sizes (0.04 – 0.4 μm), whilst PES and PS membranes are mainly in the ultrafiltration range (0.04 – 0.05 μm), and PTFE, PE and PP in the microfiltration range (0.08 – 0.4 μm). Whilst the relatively low cost polyolefinic HF membranes (PE and PP) are provided at relatively small filament diameter (<1 mm), their wider pore size

distribution and lower pore density tend to make them more susceptible to fouling (Chapter 3).

- Research in MBR technology has been growing roughly exponentially at a rate of 20% *per* year with respect to publications, compared to market growth at 11-13% *per* year. This compares to a publication exponential growth rate 45% *per* year for micropollutants, driven by legislation. Fouling remains the most significant topic, featuring on 31% of all MBR papers published to end 2009 with the number of MBR papers featuring fouling growing exponentially by 1% *per* year (Chapter 4).

- Over half of the technologies originate from East Asia, with Germany providing most of remaining products. The global market value for MBRs value doubled between 2000 and 2005 (reaching $217 by this date) and is expected to increase to $488 million in 2013. The increasing acceptance of and confidence in this technology is reflected by the increase in the number of large plants, the increasing number of product suppliers with large plants (12 suppliers with at least one installation of >10,000 m^3 d^{-1} capacity), and the decrease in the gestation time between product launch and its implementation at this large scale (Chapter 3; Chapter 4).

- A practitioners survey reveal that the main technical challenges preventing MBRs from working as they should to be screening and pre-treatment, followed by clogging – as relating largely to poor screening. Overloading and under design were also identified as being challenges, these aspects then leading to fouling. This suggests that the academic research does not effectively address the practical challenges faced by MBR technology. Moreover, standardisation/interchangeability of modules with respect to their dimensions and bulk packing density is poor (Chapter 4).

Pilot-scale trials conducted to assess the performance of five different hollow fibre membranes revealed:

- Flux-step trials on the three individual membrane modules fitted in a single cassette revealed the permeability of the two outer membrane modules to be lower than that of the central one, indicating that tests are most representative if conducted on the central module. The locality of the neighbouring modules formed a channel directing the air bubbles pass the membrane fibres and this preventing their dissipation into the bulk liquor (Chapter 8).

- Flux and aeration step trials conducted on the central module revealed critical fluxes ranging from 8.4 up to 14.5 l m^{-2} h^{-1} for intermittent aeration depending on the membrane module. Values were lower in comparison to those reported from pilot-scale trials of other HF membranes operated under similar conditions (15-45 l m^{-2} h^{-1}). For continuous aeration, measured critical fluxes were slightly higher at 12-17 l m^{-2} h^{-1} (Chapter 8; Chapter 9).

- The aeration-step method revealed that for constant flux operation there was a $SAD_{m,crit}$ value below which a significant increase in membrane fouling arose, analogous to the critical flux trends. $SAD_{m,crit}$ can thus be used to optimise the aeration rate for immersed HF membrane systems. The $SAD_{m,crit}$ for both intermittent and continuous aeration regimes (0.19-0.25 and 0.06 Nm^3 h^{-1} m^{-2} respectively) was lower than the aeration rate used to identify the critical flux through flux-step experiments (0.24 and 0.48 Nm^3 h^{-1} m^{-2} respectively). This implies that the operating conditions identified for critical flux-step experiment are overly conservative. However, this was observed when the bioreactor aeration was operating; when biological aeration was stopped the opposite trend was observed with higher values of $SAD_{m,crit}$ (0.35-0.39 and 0.59-0.99 Nm^3 h^{-1} m^{-2} for intermittent and continuous aeration, respectively) being recorded. Clearly, in the absence of bioreactor aeration, the aeration supplied by

the integrated membrane aerator created insufficient shear stress to effectively scour the membrane surface (Chapter 8; Chapter 9).

- Vigorous aeration is thought to increase sludge fouling propensity through shearing of the flocs and subsequently releasing fouling material. However, the measurement of CST, SMP and supernatant turbidity, three key parameters thought to provide an indication of sludge fouling propensity, appear to correlate poorly with fouling rate: the trend observed was counter-intuitive. This was attributed to the complexity of the wastewater, and subsequent sludge characteristics, combined with the changing operating conditions and membrane systems (Chapter 9).

- In the absence of bioreactor aeration, the aeration-step trials under the two different aeration regimes revealed that, for any given SAD_m, intermittent aeration was more effective at controlling the fouling rate than continuous aeration, which is in agreement with industry practice. However, the SAD_m values recorded were generally higher than those reported for a number of full and pilot-scale applications (Chapter 9).

- There are several methodologies to estimate the critical flux; protocols currently employed for its measurement may provide an over conservative critical flux value. The measurement of $SAD_{m,crit}$ by aeration stepping offers a more appropriate method to indentify a more sustainable and low cost operation conditions of an MBR, particularly for most full-scale plant where operation is invariably below the critical flux (Chapter 8; Chapter 9).

10.2 Future work

It is suggested that the pilot-scale experiments are modified thus:

- A larger module frame to support more than 3 modules, allowing experiments to be performed on multiple central modules fitted with different test membrane characteristics. This is likely to provide a more consistent test protocol than that employed in the current study.

- Further automation to allow the introduction of backwash cycles, and filtration step length and height.

Moreover, further trials are needed on full-scale installations to verify the impact of the bioreactor aeration on both critical flux and aeration. It is suggested to perform long term steps to evaluate fouling rate and membrane permeability of the different membrane modules. As for the critical aeration demand test, the same range of fluxes tested during the critical flux determination should be tested at each individual aeration step.

Given the results of the practitioner's survey, academic research should work more in alliance with the practioners issues in order to ameliorate this technology. Therefore, more attention should be given to screening and clogging.

Further work should be carried out on the sidestream modules. The sidestream configuration is easier to access from both operational and maintenance perspective when cleaning or replacing is required. The tests performed with sidestream modules, although without success, provided useful information and a few suggestions can be withdrawn for a more comprehensive and optimisation of the sidestream operation. In order to reduce the pumping cost hence the energy costs, the impact of the liquid flow on membrane permeability must be verify, and compared with airlift regime, with appropriate modification in the pilot plant such as sludge flow meters, allowing a more accurate control of the sludge flow.

APPENDICES

APPENDIX A FATE AND BEHAVIOUR OF COPPER AND ZINC IN SECONDARY BIOLOGICAL WASTEWATER TREATMENT PROCESSES: I EVALUATION OF BIOMASS ADSORPTION CAPACITY

Richard S. Crane[1], Paul Barton[2], Elise Cartmell[2], Frederic Coulon[3], Peter Hillis[4], Simon J. Judd[2], Ana Santos[2], Tom Stephenson[2] and John N. Lester[2]

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[1]Integrated Alliance, Great Sankey, Warrington, Cheshire, WA5 3LP, UK
[2]Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK
[3]Centre for Resource Management and Efficiency, Cranfield University, MK43 0AL, UK
[4]United Utilities, Great Sankey, Warrington, Cheshire, WA5 3LP, UK

Abstract

The current sources of copper and zinc in municipal wastewaters have been considered and the change in the concentrations and quantities of these two elements entering sewage treatment works over the last three decades calculated. The concentrations and quantities of the heavy metals, cadmium, chromium, copper, mercury, nickel, lead and zinc entering UK sewage treatment works have been reduced by between 50 and 90% during this period. However, copper and zinc appear to exhibit improvements at the lower end of these ranges and appear to remain a cause for concern, particularly their concentrations in sewage effluents and their potential environmental impacts on receiving waters. Bench studies have been undertaken to predict removals by three types of biological wastewater treatment plants, trickling filters, conventional activated sludge and membrane bioreactors to determine if any of these processes are more efficacious in removal of these metals. These results suggest that despite membrane bioreactor biomass achieving the lowest

effluent suspended solids concentration and having the lowest effluent chemical oxygen demand, which is accepted as a surrogate measure of organic chemical chelating ability of the aqueous phase, they produce the highest effluent values for the two metals in this study (copper and zinc). Removals of zinc and copper in biological wastewater treatment processes are probably primarily determined by those factors influencing metal solubility in the biomass matrix.

A.1 Introduction

The presence of so-called “heavy metals” in municipal wastewater has been the subject of concern for over six decades. Initially adverse impacts on biological wastewater treatment processes were the primary issue (Brown and Lester, 1979; Lester, 1983; Stones, 1977; Lester, 1987a; Lester, 1987b; Bailey *et al.*, 1970; Barth *et al.*, 1965; Blok, 1976). As trade effluent regulation was introduced to control industrial discharges of heavy metals to sewer, emphasis shifted to the adverse impacts of heavy metal contaminated sludges applied to agricultural land *i.e*. soil fertility, crop production and consumer exposure (Lester, 1987b; Lester *et al.*, 1983; Sterritt and Lester, 1980c; Lake *et al.*, 1984; ADAS (Agricultural Development and Advisory Service), 1971; Cantwell *et al.*, 1982; Cheng *et al.*, 1975; Rudd *et al.*, 1988; Berrow and Webber, 1972; Collinge and Bruce, 1981; Calcutt and Moss, 1984; The Olso and Paris Commissions, 1985; Thompson, 1982). Further source control abated these concerns. However, the ubiquitous nature of these elements arising from domestic sources (Table Appendix A.1) suggests that it is inevitable that their concentrations cannot be significantly reduced further by trade effluent control.

Table Appendix A.1 Typical sources of metals into sewage treatment works as demonstrated by Henriksdal WwTW in Stockholm (adapted from Sörme and Lagerkvist, 2002)

Sector	Goods/Activity	Relative Contribution to Total Element Quantity, %	
		Cu	Zn
Households	Food	4.5	25
	Laundry Detergent	0.0	0.1
Households & Businesses	Pipes & Taps	66	6.6
	Drinking Water	3.2	1.3
Businesses	Large Enterprises	1.4	1.9
	Car Washes	4.8	22
Traffic	Brake Linings	4.5	0.6
	Tyres	0.0	8.9
	Asphalt	0.2	0.5
	Oil	0.0	0.4
Buildings	Copper Roof	13	
	Galvanised Sheet		24
	Drainage Water	2.0	4.4
Atmospheric Deposition		0.4	2.4
Chemical treatment		0.0	2.4

Therefore, heavy metals in sewage effluents still remain a concern as a consequence of their adverse impacts on the biota and sediments of the receive waters and of the hydrosphere in general (Kirk and Lester, 1984; European Commission, 2006; European Commission, 2000; European Commission, 1986; European Community, 1976). Whilst these elements are only present in concentrations of μg l^{-1} and in some case ng l^{-1} (Ziolko *et al.*, 2010) the potential magnitude of the problem is perhaps best appreciated when the masses of these elements discharged *per annum* are estimated. Such an estimate was calculated for the United Kingdom based on data gathered in the 1970's and published in 1983 (Lester, 1983) using information then available (Table

Appendix A.2). This suggested that at that time 12,508 tonnes of the toxic elements (Cd, Cu, Cr, Ni, Pb and Zn) were discharged to sewer each year, based on the annual flow of crude sewage in the UK (Ministry of Housing and Local Government, 1970) and average heavy metal concentrations in the influent crude sewage at a typical urban wastewater treatment works (Lester *et al.*, 1979; Stoveland *et al.*, 1979b; Lewin and Rowell, 1973; Stoveland *et al.*, 1979). Because of the limited information on heavy metal concentrations in crude sewage the veracity of this calculation was tested by a second independent calculation using the annual sludge production for the UK (Department of the Environment and National Water Council, 1977), and average concentrations of heavy metals in sewage sludges determined in two surveys of UK sludges (Berrow and Webber, 1972; Sterritt and Lester, 1980b) and assuming 75% removal of all heavy metals during wastewater treatment (Lester *et al.*, 1979; Stoveland *et al.*, 1979b; Stoveland *et al.*, 1979; Oliver and Cosgrove, 1974). This independent calculation suggests an annual discharge of *c.* 10,481 tonnes per annum of heavy metals in crude sewage, remarkably good agreement give the limited nature of the data in the 1970s. A reduction in the quantity of total heavy metals of an order of magnitude was observed between the 1970s and 2006 which is discussed later.

Table Appendix A.2 Comparison of annual concentrations and quantities of heavy metals in crude sewages, effluents and sludges of England and Wales between 1970s (data collected between 1970-1976) and 2006.

Metal	Typical Concentration in Crude Sewage, μg l^{-1}		Total in Sewage, t yr^{-1}		Typical Concentration in Sludges, mg kg^{-1} DS		Total in Sludges, t yr^{-1}	
	1970(s) (A)	2006 (B)	1970(s) (C)	2006 (C*)	1970(s) (D)	2006 (E)	1970(s) (F)	2006 (G)
Cd	6.5	0.76	33	3.1	25	3.4	31	6.1
Cr	60	12.4	307	49.8	843	163	1,045	291
Cu	295	77.8	1,507	312.4	845	565	1,048	1008
Pb	395	25.3	2018	101.6	1185	221	1,496	394
Ni	40	14.2	204	57	400	59	496	105
Hg	1.64(J)	0.54	8.4(I)	2.2	5.1(J)	2.3	6.3	4.1
Zn	1650	155.4	8431	623.9	3015	802	3,739	1,431
	Total in Sewage measured, t yr^{-1}		12,508	1,150	Total in Sludge measured, t yr^{-1}		7,861	3,239
	Total in Effluent, t yr^{-1} (H)		3,127	288	Total in Effluent, t yr^{-1} (H)		2,620	1,080
	Total in Sludge (by calculation) (H)		9,381	863	Total in Sewage (by calculation) (H)		10,481	4,319

A: Mean values from Lester *et al.,* (1979), Stoveland *et al.*, (1979) and Lewin and Rowell (1973)
B: Rule *et al.*, (2006)
C: Daily flow of sewage $14x10^6$ m^3 d^{-1} (Ministry of Housing and Local Government, 1970)
C*: Daily flow of sewage $11x10^6$ m^3 d^{-1} (DEFRA, 2002)
D: Mean values of concentration means given by Berrow and Webber, (1972) and Sterritt and Lester, (1980c)
E: Gendebien *et al.*, 1999
F: Annual quantity of sludge produced $1.24x10^6$ tds (Department of the Environment and National Water Council, 1977)
G: Annual quantity of sludge produced $1.78x10^6$ tds (Water UK, Water UK Sustainability Indicators 2007/08)
H: Assuming 75% overall removal efficiency for these metals (Oliver and Cosgrove, 1974).
I: ENDS, 1991
J: Mercury crude sewage and sludge concentration data were obtained through back calculation from the total in sewage value and total in sludges value.
DS: Dry Solids

During conventional wastewater treatment heavy metal removal occurs during both primary sedimentation and secondary biological treatment (Brown and Lester, 1979; Lester, 1983; Lester *et al.*, 1983; Lester *et al.*, 1979; Stoveland *et al.*, 1979b; Stoveland *et al.*, 1979; Kempton *et al.*, 1987b; Kempton *et al.*, 1987a). Removal during primary sedimentation is a physical process, dependent on the settlement of precipitated metal or the association of soluble or insoluble non-settleable metal with settleable solids. Minimal removal of soluble metals occurs during this process and the proportions of soluble to total metal in the effluent (settled sewage) increases as a result (Lester *et al.*, 1979; Goldstone *et al.*, 1990a; Goldstone *et al.*, 1990c; Goldstone *et al.*, 1990b). It has been recently reported that the return of sludge liquors to the crude sewage can enhance metal removal during primary sedimentation at least for copper (Ziolko *et al.*, 2009). Whilst storm flow conditions cause deterioration in removal of most metals (Rossin *et al.*, 1983) with the exception of nickel where no change was observed. The presence of synthetic organic chelating agents such as nitrilotriacetic acid may also adversely impact upon heavy metal removal (Stoveland *et al.*, 1979b; Stoveland *et al.*, 1979a).

For metal removal to occur during secondary treatment the metal must associate with settleable solids which are removed from the effluent by gravity during secondary sedimentation. Metal removal is potentially of two types (Brown and Lester, 1979):

- Settlement of insoluble metal;
- Adsorption of soluble metal or fine particulate metals by the sludge flocs.

It has been proposed that the greater efficiency of the activated sludge process in metal removal is due to the greater efficiency of suspended solids removal and hence insoluble metal removal in secondary sedimentation tanks than in primary sedimentation tanks (Brown *et al.*, 1973; Chen *et al.*, 1974). Whilst, it has been proposed (Brown and Lester, 1979), that some insoluble metal particulates can settle on their own, it is difficult to distinguish in practice between precipitated metals which have settled independently, but are removed

with sludge, and precipitated metals which have interacted with the floc matrix and become physically entrapped and settled with the sludge flocs (Ziolko *et al.*, 2010).

It is evident that factors which enhance metal solubility will prevent precipitation and also binding to the biomass. These factors can be influenced by operating parameters and may be divided into (Lester, 1983):

(1) Physical

a. Temperature
b. pH
c. Metal solubility
d. Redox

(2) Chemical

a. Concentration of natural and synthetic complexing agents
b. Metal concentration
c. Valency

(3) Biological

a. Concentration of complexing agents generated by the biomass
b. Products of cell lysis
c. Extracellular polysaccharides

(4) Operating Parameters

a. Stirred sludge volume index (SSVI)
b. Sludge age
c. Suspended solids removal
d. Mixed liquor suspended solids concentration (MLSS)
e. Dissolved oxygen concentration
f. Efficiency of secondary solids removal.

The complex nature of sewage makes it difficult to define the precise chemical forms (species) of metals present. They could potentially occur in one or more of the following forms:

1. Soluble organic metal complexes
2. Free metal ions
3. Cell bound metal (polymer/active uptake)
4. Chemical precipitates
5. Insoluble metal complexes (bound to biomass).

Numbers 3, 4 and 5 are particulate and may be removed as settleable solids. Numbers 1 and 2 may not be removed unless transformed into one or more of the other settleable forms.

In a study of crude sewages Cantwell *et al.*, (1982) found that in six out of seven samples there was less than 1% of the nickel bound to organics in the dissolved phase. This could also be the case for other metals (Sterritt and Lester, 1985) suggesting that much of the soluble metal in sewage is complexed by soluble organic ligands. The extent to which this may occur is controlled by the complexation capacity of the matrix (Stephenson and Lester, 1987a). In the case of copper and nickel the complexation capacity of crude sewage and final effluent has been found to exceed the total concentration of those metals present (Cantwell *et al.*, 1982; Laxen and Harrison, 1981) suggesting again that only very small quantities of these metals would be in the ionic form. Metals which are largely complexed by soluble organic ligands may only be removed if these complexes dissociate to form species which have a higher affinity for the biomass. It has been demonstrated that the affinity of copper for activated sludge extracellular polymers (Rudd *et al.*, 1983b) as determined by its stability constant is greater than that of cadmium and nickel. Thus copper may dissociate from its soluble complexes to be removed by association with biomass, whereas nickel has an affinity for the soluble phase of

sewage comparable to copper (Cheng *et al.*, 1975) but a weaker affinity for the biomass and is therefore removed to a lesser degree.

The removal of insoluble metal can be strongly influenced by particle size. Chen *et al.*, (1974) observed that 50% of the copper and zinc in sewage was adsorbed to particles greater than 8 μm in diameter and these were very effectively removed. Whilst 50% of the nickel and lead were associated with particles less than 8 μm in diameter and these were poorly removed.

This study has been undertaken to determine the absorptive capacity of three types of biological secondary sewage treatment processes, trickling filters (TF), activated sludge (AS) and membrane bioreactors (MBR) and the biomass that they develop. Zinc and copper, two of the most abundant heavy metals in crude sewage and final effluent, have been selected for this study because of their potential effects on receiving waters (European Commission, 2000; US EPA, 2006).

A.2 Materials and Methods

A.2.1 Sources of biomass

To determine the adsorptive capacity of biomass developed in different types of secondary biological treatment processes, samples were collected from: (1) a full-scale trickling filter (TF) plant located at Cranfield University in the South East of England, UK; (2) a conventional activated sludge (AS) pilot plant; and (3) a membrane bioreactor (MBR) pilot plant both operated on the same site in the pilot plant hall at Cranfield University. By doing this the effect of sewage type, composition and associated variations in strength were eliminated, as all three processes were operated on the same settled sewage from the primary sedimentation tanks of the Cranfield University works which served a population equivalent (p.e.) of 2,500 with a trade input of <10%. The operating regimes for the plants are as described below.

A.2.2 Trickling filter full-scale wastewater treatment works operating regime

The biomass from the full-scale plant was collected from the top of a 108 m^3 humus tank. The humus tank feed was from a nitrifying trickling filter (204 m^3) receiving settled sewage from a 108 m^3 primary settlement tank. The trickling filter was a non-submerged fixed-film reactor using BIOdek® plastic media with continuous wastewater distribution. The HRT was *c.* 30 minutes and the dry weather flow was 675 m^3 d^{-1}. The humus sludge suspended solids concentration was 1,513 mg l^{-1}.

A.2.3 Activated sludge pilot plant operating regime

The pilot-scale AS plant operated at Cranfield University contained a 2 l working volume pre-anoxic zone with a 30 l working volume aerobic tank which was completely mixed and a separate final settlement tank (FST) for secondary clarification. The activated sludge plant was operated with a HRT of 8 hours and a SRT of 12 days. The MLSS was 2,725 mg l^{-1}. Activated sludge biomass was collected from the aerobic tank.

A.2.4 MBR pilot plant operating regime

The pilot-scale MBR plant comprised a 2200 l sludge process tank equipped with submerged hollow fibre membranes with a 17.5 m^2 surface area and 0.03 µm pore size (Asahi Kasei, Tokyo, Japan). The HRT was 14-15 hours. The mixed liquor suspended solids concentration was 9,718 mg l^{-1} and the SRT >40 days. The biomass was collected from the process tank.

The composition of the settled sewage influent and typical effluent quality from the pilot AS and MBR units and the full-scale TF plant are outlined in Table Appendix A.3.

Table Appendix A.3 Settled sewage and final effluent concentrations for standard determinants for the full-scale trickling filter plant and pilot-scale activated sludge and membrane bioreactor plants, all operated on the same settled sewage

Parameters	Trickling Filter	Activated Sludge	MBR
HRT, hrs	0.5	8	14-15
SRT, days	nd	12	>20-100
Temperature, ºC	18	18	18
Settled Sewage			
COD, mg O_2 l^{-1}		508	
NH_4, mg N l^{-1}		23.3	
NO_3, mg N l^{-1}		5.7	
TSS, mg l^{-1}		141	
pH		7.93	
Effluent			
COD, mg O_2 l^{-1}	78.2*	69	42
NH_4, mg N l^{-1}	5*	2.8	0.4
NO_3, mg N l^{-1}	nd	11.2	34.0
TSS, mg l^{-1}	17.2*	15	nd
pH	7.5*	7.5	6.1

nd: not determined, *effluent post humus tank not as discharged effluent

A.2.5 Bench studies to evaluate biomass metal adsorptive capacity

Aliquots of each biomass (150 ml) were placed in 250 ml conical flasks and spiked with Cu and Zn stock solutions (10,000 mg l^{-1} atomic absorption standards solutions from Fisher Scientific, Loughborough, UK) to achieve concentrations of 0, 10, 20, 30 and 40 µg l^{-1} for Cu and 0, 100, 200, 300 and 400 µg l^{-1} for Zn. All treatments were in duplicate. The samples were mixed using an orbital shaker (Stuart model SSL1, Fisher Scientific, Loughborough UK) at 125 oscillations *per* minute for periods of 30 minutes, 3 hours and 24 hours at a temperature of 20±1°C. The samples were then centrifuged at 500 *g* in a centrifuge (Sorvall Stratos, DJB Labcare, Newport Pagnell, UK) for 30 minutes. The centrate was decanted and filtered through 0.45 µm cellulose nitrate membranes (Anachem, Bedfordshire, UK) prior to metal analysis.

Further experiments of an identical nature were undertaken in which the biomass was normalised to 2,000 mg l^{-1} SS by either consolidation or dilution. The biomass was normalised by measuring the initial sample SS followed by diluting the sample with final effluent (FE) for the AS and MBR biomasses and consolidation by gravimetric settling for the TF biomass.

A.2.6 Metal analysis

The glass and plastic ware used for collection, storage and manipulation of samples was soaked for a minimum of 1 hour in a 3% v/v Decon 90 (Fisher Scientific, Loughborough, UK) detergent solution prepared in ultrapure water (18.2 MΩ water PURELAB Ultra water purification system, ELGA, High Wycombe, UK) and then rinsed with the same source of ultrapure water. Subsequently they were soaked for a minimum period of 1 hour in a 1% v/v Primar Plus trace analysis grade nitric acid (Fisher Scientific, Loughborough, UK) prepared again in ultrapure water and following a final rinse in ultrapure water they were air dried.

Total metal analysis was undertaken on 30 ml samples placed in digestion tubes and acidified with 1.5 ml Optima ultra pure grade nitric acid (Seastar Chemicals Inc., Pittsburg, PA, USA). The samples were then digested in a MARSXpress microwave digester (CEM Microwave Technology, Buckingham, UK) to pre-set sample dissolution EPA method 3015 (US EPA, 2007). Every set of digested samples included a sample of Certified Reference Material (CRM) – BCR-144R Sewage sludge of domestic origin (Laboratory of the Government Chemist, LGC, Teddington, UK). The samples were then transferred to 250 ml centrifuge tubes for analysis. Following digestion, the Cu samples were analysed using atomic absorption spectrophotometry (AAnalyst 800, Perkin Elmer Ltd., Beaconsfield, UK) equipped with a Zeeman-corrected transversely-heated graphite atomiser (THGA) and an AS-800 auto sampler. The Zn samples were analysed using the same AAnalyst 800 spectrophotometer using a burner system and an AS-90 auto sampler. The analytical conditions were those recommended by Perkin Elmer, utilising a multi-element hollow cathode lamp for both Cu and Zn and in all other respects analytical procedures conformed to those previously described (Sterritt and Lester, 1980a).

Samples for total metal analysis should contain a maximum of 100 mg of solids, if the sample contained more than 100 mg of solids; dilution with acidified ultrapure water was used to reduce the solids content to $\leq$100 mg. Batches of duplicate blanks, unspiked samples and samples spiked at low and high standard additions were analysed to determine accuracy, variability and to characterise the method performance. Both total and dissolved samples, spiked at low and high additions exhibited no significant differences within or between batches with an overall recovery of 100% for both metals. To confirm the accuracy of the digested total metal samples, the Cu and Zn concentrations of the digested CRM sample were compared with its certified value and sample results and no adjustment was required for incomplete digestion as determined by the CRM value.

For dissolved metal analysis each sample was vacuum filtered through a Millipore all glass three piece vacuum filtering set (Millipore, Cambridge, UK) using a 0.45 µm pore size cellulose nitrate membrane filter (Anachem Ltd., Bedfordshire, UK). An aliquot of 30 ml (±0.1 ml) of the sample filtrate was then placed in a 50 ml centrifuge tube and acidified with 0.75 ml (±0.1 ml) of 2.5% volume Optima grade ultra pure nitric acid. Following acidification the samples were analysed by atomic absorption spectrophotometery as per total metals.

A.2.7 Suspended solids analysis

Total suspended solids analysis was determined within four hours of sample collection according to Standard Method 2540D (APHA, 1998) using grade GF/D glass microfibre filter papers (Whatman, Maidstone, UK).

A.2.8 Chemical oxygen demand

Determination of COD was carried out using a Merck Spectroquant (Nova 60 Spectrophotometer VWR International Ltd, Dorset, UK) COD cell test with the range of 500-10,000 mg COD l^{-1} (VWR, International Ltd, Dorset, UK). For soluble COD the samples were centrifuged at 12,000 *g* in a Rotanta 96 R centrifuge (Hettich Zentrigugen, Tuttlingen, Germany) for 20 minutes. The centrate was then decanted and filtered through a 0.45 µm pore size glass microfibre filter paper (Whatman, Maidstone, UK) prior to analysis.

A.2.9 Ammonium analysis

The analysis of ammonium (NH_4^+) was carried out using Merck Spectroquant Ammonium cell test having a range of 0.01-80 mg l^{-1} NH_4-N (VWR, Leicestershire, UK) using the method analogous to Standard Method 4500-NH_3D (APHA, 1998).

A.2.10 Nitrate

Nitrate analysis was carried out using Merck Spectroquant nitrate cell test 0.5-50 mg l^{-1} NO_3-N (VWR, Leicestershire, UK) using the method analogous to (ISO, 1985).

A.2.11 Temperature

The wastewater temperature was measured using a mercury in-glass-thermometer -10°C to +110°C (VWR International Ltd, Dorset UK).

A.2.12 Dissolved oxygen

The dissolved oxygen (DO) was determined using the Hach HQ20 meter equipped with a Luminescent Dissolved Oxygen (LDO®) probe (Hach Lange Ltd, Manchester, UK).

A.2.13 Total BOD analysis

The BOD was determined based on Methods for the Examination of Water and Associated Materials (Standing Committee of Analysts, 1988). The added seed was 5 ml final effluent per 500 ml of dilution water. Diluted samples were transferred to glass BOD bottles (Fisher Scientific, Lougborough, UK) and the dissolved oxygen determined using a Hach LDO meter (Camlab, Cambridge UK).

A.3 Results

A.3.1 Adsorptive capacity of activated sludge mixed liquor, humus and membrane bioreactor biomass for copper and zinc

Batch experiments were undertaken as described above, each biomass was spiked at four concentrations, 10, 20, 30 and 40 μg l^{-1} for copper and 100, 200, 300, 400 μg l^{-1} for zinc these being indicative of concentrations occurring in settled sewages. The duplicate treatments plus blanks (containing only the indigenous concentration) were incubated for 30 minutes, 3 hours and 24 hours. These time periods were selected to cover the range of potential hydraulic retention times which could be encountered at full-scale in the three types of biological treatment processes under study namely trickling filters, activated sludge and MBRs.

The soluble metal concentrations following sample filtration (0.45 μm) are presented in Figure Appendix A.1. It can be seen that the adsorbed copper concentrations for the different biomass types followed the order AS (99%)>TF (84%)>MBR (47%). Whilst for zinc the adsorbed concentrations for the different biomass types followed the order TF (84%)>AS (68%)>MBR (50%). However, for both metals the highest soluble concentrations were found in the filtrates from the MBR biomass suggesting that this unit treatment process would give the poorest removal for both elements. This result may appear surprising given that the biomass concentration of the MBR was the highest at 9,717 mg l^{-1} compared to that of the activated sludge process of 2,725 mg l^{-1} and the trickling filter of 1,512 mg l^{-1}. However, the adsorbed indigenous concentration of both elements was also highest in the MBR biomass (50.2 μg kg^{-1} for copper and 52 μg kg^{-1} for zinc; Table Appendix A.4) reflecting the very high solids residence time (>30 days) and consequently the very low wastage rate. This compares with the activated sludge indigenous adsorbed biomass concentration of 27.9 μg kg^{-1} and 24.86 μg kg^{-1} for copper and zinc respectively and 29.8 μg kg^{-1} and 26.06 μg kg^{-1} for trickling filter (humus) adsorbed copper and zinc concentrations.

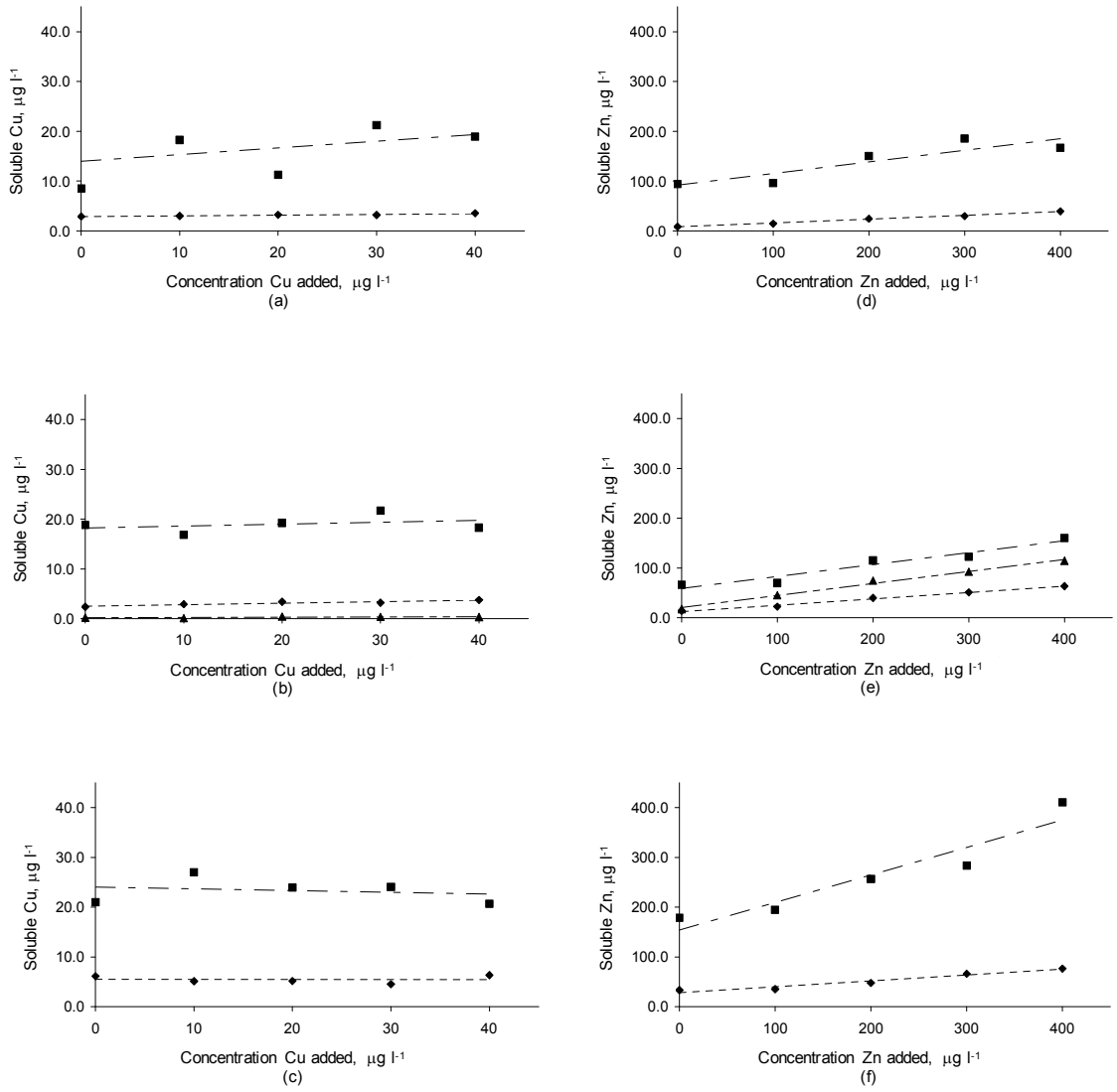

Figure Appendix A.1 Adsorptive capacity of biomass taken from a AS (▲), MBR (■) and TF (♦) for soluble Cu mixed for (a) 30 minutes (MBR and TF), (b) 3 hrs (AS, MBR and TF), (c) 24 hrs (MBR and TF) and for soluble Zn mixed for (d) 30 minutes (MBR and TF), (e) 3 hrs (AS, MBR and TF) and (f) 24 hrs (MBR and TF)

The residual COD for the different biomass types was 42 mg l^{-1}, 55 mg l^{-1}, 33 mg l^{-1} for the TF, AS and MBR biomasses respectively. Chemical Oxygen Demand can be used as a surrogate measure for complexing agents, both natural and synthetic, which could act to enhance metal solubility thereby reducing adsorption and hence removal from the final effluent (Table Appendix A.3). The COD value for the MBR was lower than the TF and AS although the metal removal was the poorest. This suggests that it is not the total COD which is critical in determining metal solubility, but rather specific components present in the MBR which appear to be very effective in solubilising both copper and zinc and minimizing their removals. These particular components of the MBR aqueous phase were presumably synthesised by the MBR biomass since they were not present in the influent settled sewage.

Table Appendix A.4 Percentage mass of copper and zinc adsorbed in batch studies by AS, TF and MBR biomass at varying mixing periods and over a range of concentrations

	AS Biomass			Tricking Filter Humus Biomass			MBR Biomass		
	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed
Phase	Soluble			Soluble			Soluble		
30 minutes mixing – Cu									
0 µg l^{-1} spike	n/d	n/d	n/d	2.39	n/a	n/a	18.82	n/a	n/a
10 µg l^{-1} spike	n/d	n/d	n/d	2.92	0.53	76.4	16.84	-1.98	41.6
20 µg l^{-1} spike	n/d	n/d	n/d	3.40	1.01	84.8	19.24	0.42	50.4
30 µg l^{-1} spike	n/d	n/d	n/d	3.20	0.81	90.1	21.71	2.89	55.5
40 µg l^{-1} spike	n/d	n/d	n/d	3.75	1.36	91.2	18.28	-0.54	68.9
Mean (Cu)				*3.13*	*0.93*	*85.63*	*18.98*	*0.20*	*54.1*
SD (Cu)				*0.51*	*0.35*	*0.07*	*1.78*	*2.05*	*0.11*
3 hrs mixing – Cu									
0 µg l^{-1} spike	0.19	-0.06	98.7	2.90	n/a	n/a	8.50	n/a	n/a
10 µg l^{-1} spike	0.13	0.24	97.9	2.99	0.09	76.9	18.25	9.75	1.3
20 µg l^{-1} spike	0.43	0.16	98.8	3.24	0.34	85.9	11.24	2.74	60.6
30 µg l^{-1} spike	0.35	0.16	99.1	3.18	0.28	90.3	21.23	12.74	44.8
40 µg l^{-1} spike	0.35	-0.06	98.7	3.55	0.65	91.7	18.91	10.41	61.0
Mean (Cu)	*0.29*	*0.09*	*98.64*	*3.17*	*0.34*	*0.86*	*15.63*	*8.91*	*41.93*
SD (Cu)	*0.12*	*0.14*	*0.44*	*0.25*	*0.23*	*0.07*	*5.46*	*4.3*	*28.11*
24 hrs mixing – Cu									
0 µg l^{-1} spike	n/d	n/d	n/d	6.11	n/a	n/a	21.00	n/a	n/a
10 µg l^{-1} spike	n/d	n/d	n/d	5.11	-1.00	68.3	26.99	5.99	12.9
20 µg l^{-1} spike	n/d	n/d	n/d	5.18	-0.93	80.2	23.93	2.93	41.6
30 µg l^{-1} spike	n/d	n/d	n/d	4.54	-1.57	87.4	24.09	3.09	52.8
40 µg l^{-1} spike	n/d	n/d	n/d	6.34	0.23	86.2	20.68	-0.32	66.1
Mean (Cu)				*5.46*	*-0.82*	*80.53*	*23.33*	*2.93*	*43.35*
SD (Cu)				*0.75*	*0.75*	*8.74*	*2.59*	*2.58*	*22.64*

	AS Biomass			Tricking Filter Humus Biomass			MBR Biomass		
	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed	Conc., µg l^{-1}	Absolute Change, µg l^{-1}	% Mass Adsorbed
Phase	Soluble			Soluble			Soluble		
30 minutes mixing – Zn									
0 µg l^{-1} spike	n/d	n/d	n/d	13.89	n/a	n/a	66.34	n/a	n/a
100 µg l^{-1} spike	n/d	n/d	n/d	22.16	8.26	80.5%	69.79	3.45	58.0
200 µg l^{-1} spike	n/d	n/d	n/d	39.72	25.83	81.4%	115.05	48.71	56.8
300 µg l^{-1} spike	n/d	n/d	n/d	50.96	37.07	83.8%	122.50	56.16	66.6
400 µg l^{-1} spike	n/d	n/d	n/d	63.32	49.42	84.7%	159.92	93.58	65.7
Mean (Zn)				*38.01*	*30.15*	*82.6%*	*106.72*	*50.48*	*61.78*
SD (Zn)				*20.27*	*17.48*	*1.97*	*39.19*	*36.99*	*5.09*
3 hrs mixing – Zn									
0 µg l^{-1} spike	17.33	n/a	n/a	28.56	n/a	n/a	94.28	n/a	n/a
100 µg l^{-1} spike	45.18	27.85	61.5	24.50	5.94	86.6	96.11	1.83	50.5
200 µg l^{-1} spike	74.76	57.43	65.6	24.42	15.86	88.3	150.19	55.91	49.0
300 µg l^{-1} spike	92.26	74.93	70.9	29.72	21.16	90.4	185.30	91.02	53.0
400 µg l^{-1} spike	114.60	97.27	72.5	39.39	30.83	90.4	166.79	72.51	66.3
Mean (Zn)	*68.83*	*64.37*	*67.65*	*29.32*	*18.45*	*88.93*	*138.53*	*55.32*	*54.7*
SD (Zn)	*38.37*	*29.30*	*5.05*	*6.11*	*10.39*	*1.84*	*41.47*	*38.43*	*7.91*
24 hrs mixing – Zn									
0 µg l^{-1} spike	n/d	n/d	n/d	33.24	n/a	n/a	178.89	n/a	n/a
100 µg l^{-1} spike	n/d	n/d	n/d	35.20	1.96	73.6	194.49	194.49	30.3
200 µg l^{-1} spike	n/d	n/d	n/d	47.82	14.58	79.5	256.75	256.75	32.2
300 µg l^{-1} spike	n/d	n/d	n/d	66.12	32.88	80.2	283.78	283.78	40.7
400 µg l^{-1} spike	n/d	n/d	n/d	76.59	43.35	82.3	410.65	410.65	29.1
Mean (Zn)				*51.80*	*23.19*	*78.9*	*264.91*	*286.42*	*33.08*
SD (Zn)				*19.08*	*18.49*	*3.73*	*92.22*	*90.87*	*5.24*

n/a: not applicable; n/d: not determined

To determine if the observed differences in metal adsorption were due to the difference in biomass concentrations and in particular the higher concentration of the MBR biomass (9,717 mg l^{-1}) the experiments were repeated at a standardized biomass concentration of 2,000 mg l^{-1}. This was done by diluting both the MBR and activated sludge biomass with final effluent of the respective unit treatment processes and the trickling filter biomass was consolidated by settlement. The samples were spiked and incubated as before and the results are presented for the 3 hours incubation period in Figure Appendix A.2. The trends for metal adsorption are exactly the same as in the previous experiment AS>TF>MBR for copper and TF>AS>MBR for zinc. This would strongly suggest that the controlling factor for metal adsorption was the composition of the soluble phase and in particular complexing agents, both natural and synthetic, which were present.

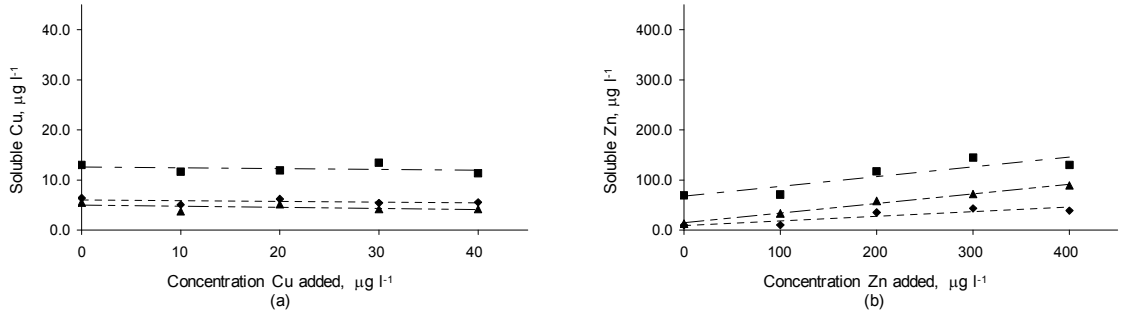

Figure Appendix A.2 Adsorptive capacity of biomass normalised to 2000 mg l^{-1} SS for AS (▲), MBR (■) and TF (♦) for 3 hrs mixing for (a) soluble Cu and (b) soluble Zn

A.3.2 Impact of process retention (incubation) time on metal adsorption

It is apparent from examination of Figure Appendix A.1 that equilibrium was achieved for both copper and zinc at all concentrations within 30 minutes. However, at the longer time period of 24 hours there would appear to have been some evidence for re-solubilisation of zinc as demonstrated by the higher concentrations in the supernatant. Re-solubilisation of copper was less pronounced, but evident. For example, the reduction in the percentage mass adsorbed for zinc for the MBR biomass was *c.* 28% between the 30 minutes and 24 hours retention time (Table Appendix A.4) and for the trickling filter biomass the reduction in the percentage mass adsorbed was 4%. In comparison the reductions in the percentage mass adsorbed for copper were 11% and 5% for the MBR and TF biomass respectively, between the 30 minutes and 24 hours retention periods. This may have been influenced by the aerobic nature of the incubation conditions causing significant biochemical changes to the biomass matrix, possibly a result of endogenous respiration or the biodegradation of extracellular polymeric material (EPM). This would be consistent with the higher soluble metal concentrations which resulted in the poor performance of the MBR where high HRT (14-15 hours) and SRT (>40 days) resulted in a biomass functioning in the endogenous respiration phase. It is the composition of the BOD/COD which is critical in determining metal solubility and it would appear that the MBR treatment process is unique in modifying the final effluent BOD composition, this would appear not to have occurred in the activated sludge and trickling filter processes examined in this study. This was probably due to the lower HRT and SRT of the activated sludge process (HRT=8 hours; SRT=12 days) and for the trickling filter (HRT= *c.* 0.5 hours, SRT indeterminate).

A.3.3 Impact of metal concentration on magnitude of adsorption

The concentration of soluble and adsorbed metal at each spiked concentration are shown in Figure Appendix A.3 for copper and Figure Appendix A.4 for zinc at the 3 hours incubation period. These corroborate the trends shown in Figure Appendix A.1 confirming that the maximum amount of soluble metal for both copper and zinc occurs in the MBR biomass. It is very evident that the lowest copper solubility occurs in the activated sludge biomass. Overall, from the concentrations of copper spiked (10-40 $\mu g\ l^{-1}$) in the activated sludge and trickling filter biomass, it is evident that all the added copper enters the adsorbed phase confirming that the TF and AS biomass was not saturated for copper and that potentially a significant reserve removal capacity exists to safeguard the environment from deleterious discharges of this element. Whilst in the case of zinc over 150 $\mu g\ l^{-1}$ of the added metal is always adsorbed. However, a significant percentage *c.* 10% of each added concentration remains in solution and suggests therefore that there is a concentration dependent function controlling metal removal for this element. Nonetheless a very significant reserve capacity exists to safeguard the environment from excessive discharges of zinc. It should be noted however that the concentrations for copper and zinc were not equivalent. The zinc concentration was ten times higher than the copper at each spike (reflecting the concentrations found in settled sewages) and therefore if the copper had been at an equivalent concentration more breakthrough may have been observed.

Despite the higher biomass concentrations in the MBR this was not the controlling factor in determining metal adsorption. The controlling factor is therefore either the nature of the biomass or the complexing capacity of the soluble phase as influenced by the biochemical activity of the biomass.

In the case of copper in the MBR biomass there is potentially a concentration effect since at the lowest added concentration of copper (10 $\mu g\ l^{-1}$) there is very little adsorption, whilst at the higher concentrations added (20-40 $\mu g\ l^{-1}$) the insoluble metal is typically 50-60% which would indicate that at these higher

concentrations the complexation capacity within the soluble phase BOD has been overcome and is unable to further solubilise the added copper.

It is evident when the percentage distributions are examined (Figure Appendix A.5 for copper and Figure Appendix A.6 for zinc) that for all concentrations studied the same percentage adsorption occurs (with the exception of copper at 10 µg l^{-1}) indicating that these effects are not concentration dependent. This would strongly suggest that there exists a very significant residual adsorptive capacity within all three types of biomass for these two elements. However, process type has a very strong influence on adsorptive capacity, since despite the very high metal concentrations present in the MBR biomass, overall removal is always inferior to that of the two other process types (TF and AS) and this strongly suggests that the biomass matrix (soluble phase) of the MBR has in some way been modified, thus enhancing metal solubility and diminishing removal.

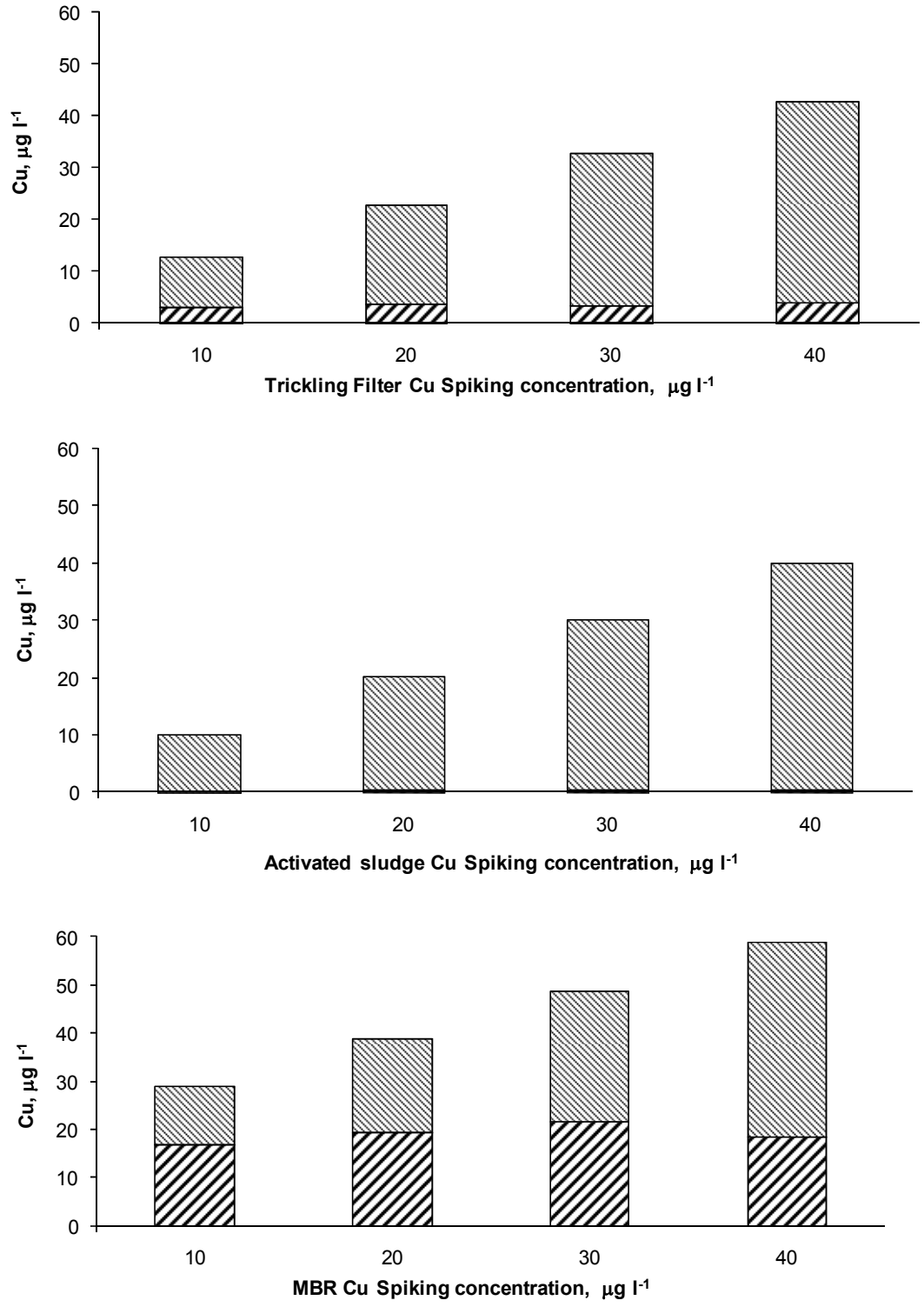

Figure Appendix A.3 The soluble and adsorbed copper concentrations in trickling filter biomass, activated sludge biomass and MBR biomass

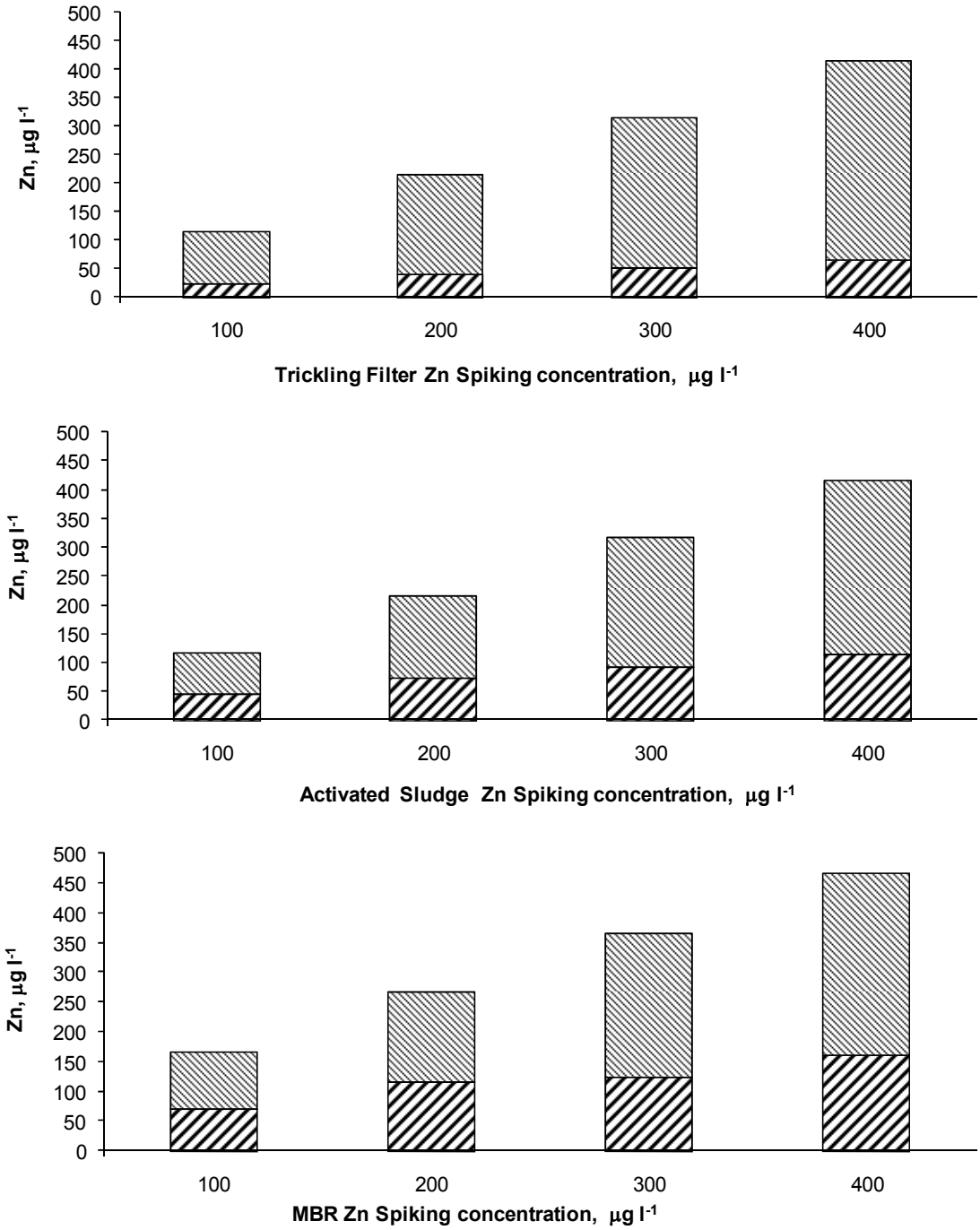

Figure Appendix A.4 The soluble and adsorbed zinc concentrations in trickling filter biomass, activated sludge biomass and MBR biomass

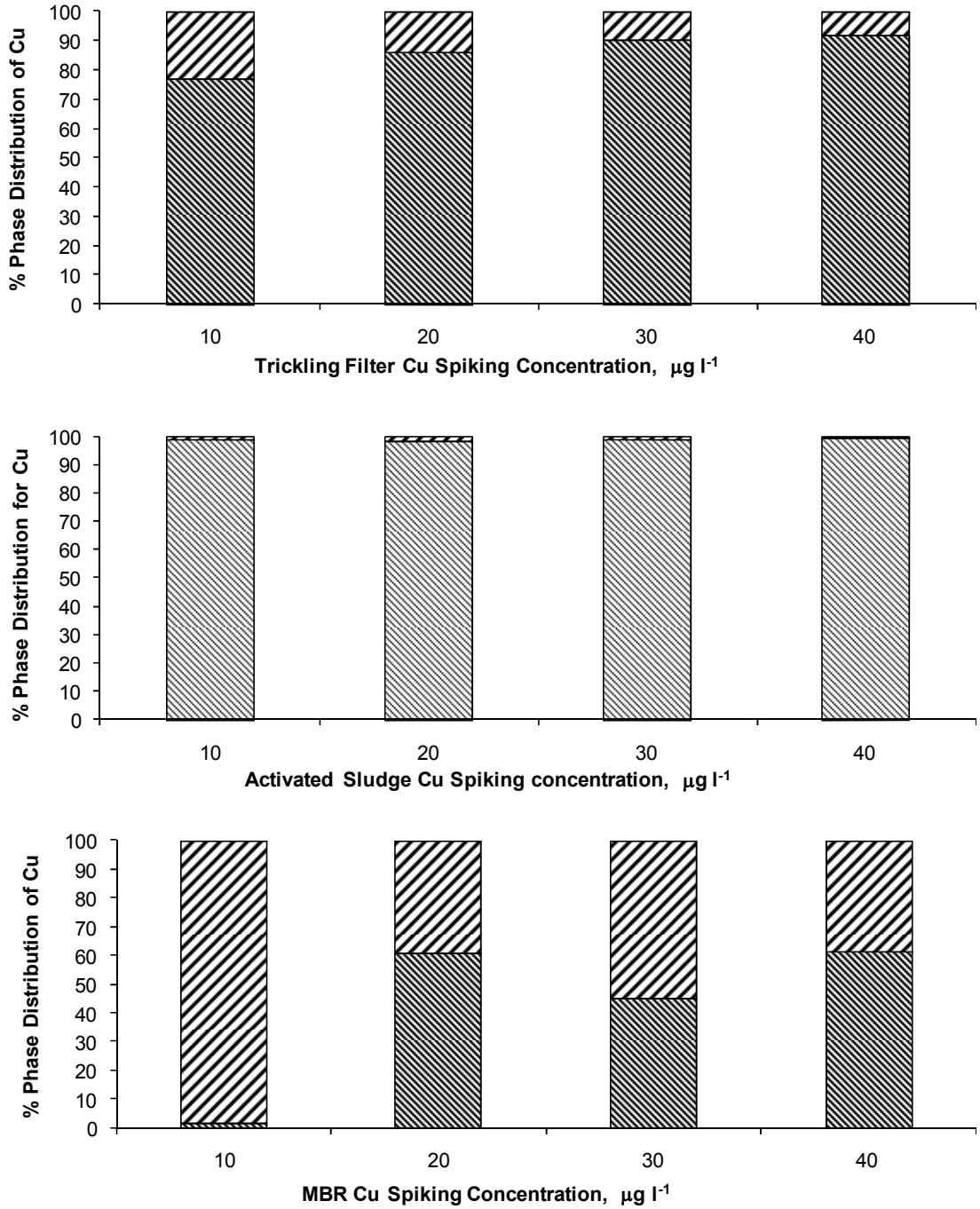

Figure Appendix A.5 The percentage phase distribution for copper in trickling filter biomass, activated sludge biomass and MBR biomass

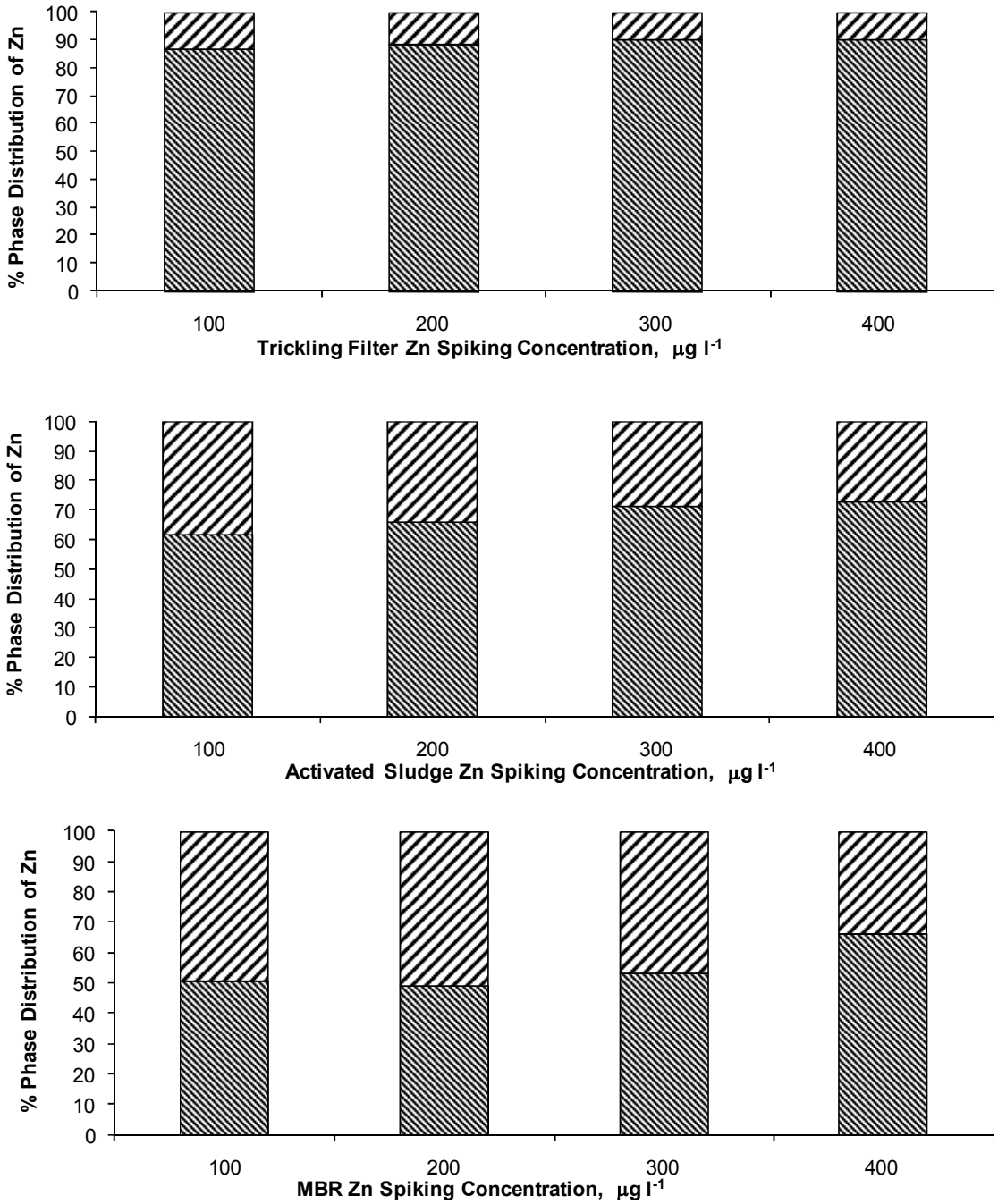

Figure Appendix A.6 The percentage phase distribution for zinc in trickling filter biomass, activated sludge biomass and MBR biomass

A.4 Discussion

Over the last thirty years progressively more stringent standards have been imposed on heavy metal concentrations in surface waters culminating in the current values reviewed by Ziolko *et al.,* (2010). This has resulted in the progressive reduction in the permissible concentrations of these elements in sewage effluents which constitute one of the major point sources to the aquatic environment (Lester, 1983; Ziolko *et al.*, 2010; Bubb and Lester, 1991). The impact of these regulations is strikingly apparent in Table Appendix A.2 for the United Kingdom. Overall quantities of most heavy metals in crude sewage have been very substantially reduced from 10,481-12,508 tonnes yr^{-1} in the 1970s to 1,150-4,319 tonnes yr^{-1} in 2006. Although there are discrepancies, particularly for the concentrations and quantities of copper and zinc. All other elements demonstrate very substantial reductions both in sewage and sludges. The anomalies in the copper and zinc data may reflect the abundance of sources for these two elements both industrial and domestic (Rule *et al.*, 2006) and their behaviour during wastewater treatment (Lester *et al.*, 1979; Davis III and Jacknow, 1975; Karvelas *et al.*, 2003; Fatone *et al.*, 2006). These anomalies coupled to their abundance are also reflected in the interest shown in their fate during wastewater treatment by the regulators (European Commission, 2000; UK TAG, 2007).

Opportunities for point source control and trade effluent regulation have almost been fully exploited. Endeavours to further reduce surface water concentrations are now increasingly focused on diffuse source abatement, which is difficult. As a consequence attention is focusing on wastewater treatment as a mechanism to further ameliorating contributions from wastewater. Whilst wastewater treatment processes were not designed for the removal of metals and micropollutants (Jones *et al.*, 2007) they do achieve significant removals of many such metals (Brown and Lester, 1979; Lester, 1983; Ziolko *et al.*, 2010) and micropollutants (Bedding *et al.*, 1983) which are now commonly referred to as hazardous substances (European Commission, 2001). However, as currently configured and operated they cannot achieve adequate protection of the aquatic

environment from hazardous substances contamination (Jones *et al.*, 2007; Koh *et al.*, 2009), although modifications may permit adequate protection in an economic and environmentally sustainable manner without recourse to such techniques as granular activated carbon (GAC) (Eilbeck and Mattock, 1987; Linstedt *et al.*, 1971) or chemical (Eilbeck and Mattock, 1987; Duan and Gregory, 2003) and electrochemical (Chen, 2004; Campbell *et al.*, 1994) recovery.

Endeavours to maximize metal removal during wastewater treatment have principally focused on secondary biological wastewater treatment (Lester, 1983; Ziolko *et al.*, 2010) since metal removal during primary sedimentation is limited to the removal of insoluble settleable particulates (Lester, 1983; Kempton *et al.*, 1987b; Rossin *et al.*, 1983; Sterritt and Lester, 1985) and given that secondary sedimentation following biological treatment is more efficient than primary sedimentation, it is the removal at this stage that is of paramount importance in determining overall metal removal (Brown and Lester, 1979). The removal of metals in the activated sludge process has been extensively evaluated, the parameters considered to be of importance in determining metal removal are mixed liquor suspended solids concentration (determined by solids retention time also referred to as sludge age) effluent suspended solids concentration and effluent biochemical and chemical oxygen demand (Kempton *et al.*, 1987b; Kempton *et al.*, 1987a; Sterritt and Lester, 1985; Kempton *et al.*, 1983; Lawson *et al.*, 1984a; Lawson *et al.*, 1984d; Stephenson and Lester, 1987b). It can be hypothesized that at high SRT (high MLSS concentration) there exists an extensive surface area or matrix to entrap or adsorb the metals present in the influent settled sewage. However, due to the low wastage rate it is feasible that the sites for metal removal may become saturated, limiting removal. Conversely at low SRT (low MLSS concentration) high wastage rates result in the rapid division of the bacterial cells which constitute the biomass, creating new uncontaminated surface area with an abundant capacity to entrap or adsorb metals, which is maintained by the removal of the metals by the high wastage rate, thus enhancing metal removal. However, SRT does not only affect MLSS concentration but, also affects effluent COD and effluent SS, with high sludge

ages favouring lower concentrations of both COD and SS in the effluent (Metcalf & Eddy Inc. *et al.,* 2003). It has been proposed that low effluent SS concentration and low effluent COD maximizes heavy metal removal in the activated sludge process (Ziolko *et al.*, 2010).

In the work reported here the partition of copper and zinc into biomass developed in an activated sludge pilot plant, a membrane bioreactor pilot plant and full-scale trickling filters has been examined. This study is unique in that all three biomass types were grown in parallel on the same settled sewage, thus eliminating sewage composition as a variable. The fate and behaviour of metals in trickling filters (humus) has been the subject of one previous study for one element (copper) in the UK (Ziolko *et al.*, 2009) although the mechanisms are assumed to be the same as those operating in the activated sludge process (Brown and Lester, 1979; Lester, 1983). Membrane bioreactors have also been the subject of limited studies (Chapter 2; Chapter 5; Chapter 6). It may be considered that trickling filters have very high SRTs (although they are not amenable to precise determination) as do MBRs and in addition the latter achieves extremely high SS removal >99%. In the studies reported here phase separation was achieved by filtration through a 0.45 µm membrane filter, which would be equivalent to an MBR and superior to the gravimetric phase separation achieved in a secondary sedimentation or humus tanks. It is clearly evident that removal as estimated by the insoluble fraction (>0.45 µm) was significantly better in the activated sludge process and the trickling filter for both copper and zinc, than for the MBR. This trend was consistent at all the concentrations of metal examined, even when the biomass concentration was standardised to avoid any bias which could have been caused by the use of the naturally occurring biomass concentration associated with each process type. This strongly suggests that the MBR operating at very high SRT (sludge age) of >40 days was generating biological molecules, not present in the influent settled sewage, which possessed the ability to chelate both copper and zinc thereby retaining them in solution, thus preventing their removal. The generation of such ligands at high sludge ages has previously been reported in the activated sludge process (Kempton *et al.*, 1983; Lawson *et al.*, 1984b; Rossin *et al.*,

1982). It would appear that the operating conditions prevailing in the activated sludge pilot plant and the trickling filter plant were not conducive to the production of these ligands. Production of biological molecules in these processes which are surface active and result in foaming has previously been reported (Ganidi *et al.*, 2009) and the production of ligands would appear to be another facet of this behaviour. It is strongly suggested by these studies that MBRs will not achieve superior metal removal to AS and TFs unless the inferior performance of secondary sedimentation tanks in solids removal compared to membranes is highly significant in determining total metal removal. Or unless the MBRs are operated at low SRTs (<12 days) not traditionally associated with this process.

That the removals observed in the activated sludge process and the trickling filter were comparable supports speculation that removal in these processes is by similar mechanisms (Brown and Lester, 1979; Lester, 1983). A very recent study which appears to be the only published study of metal removal in full-scale percolating filters, clearly demonstrates that the range of removals for copper (the only metal studied) of 22-71%, average 50% was entirely comparable to the range of values reported for the activated sludge process 55-98% average 76% for copper and for zinc 44-97% average 70% (Brown and Lester, 1979; Lester, 1983). It is also apparent from the data in Figure Appendix A.3 and Figure Appendix A.4 that the capacity of the biomass to take up these two elements is not saturated at any of the added concentrations studied and therefore a considerable residual capacity to take up these two elements remains to protect the receiving environment from contamination, which is consistent with the absorptive and partitioning behaviour previously reported for these matrices (Lawson *et al.*, 1984c; Sterritt *et al.*, 1981; Sterritt and Lester, 1981; Rudd *et al.*, 1983a; Dowson *et al.*, 1993). However, it is not clear if this potential can be employed, and if it can, what change to unit process design, configuration or management is required to access this potential. A conundrum which has been investigated quite extensively over the past thirty years (Stoveland and Lester, 1980).

A.5 Conclusions

1. Metal concentrations and quantities entering UK sewage treatment works have fallen by 50-90% over the last 3 decades. It is probable that this trend is the same in North America and in the EU and the developed world at large.

2. Copper and zinc are the two elements whose reductions in discharge to wastewater have diminished the least. This is probably significantly influenced by their diverse sources, many of which are domestic, and also their non-point source arising.

3. Removal of metals during biological wastewater treatment is critical in determining the contribution of these elements to receiving waters. The type of biological secondary treatment process employed may be important in determining these discharges.

4. In the cases of copper and zinc results from batch studies suggest that MBRs will achieve inferior removals of copper and zinc when compared to both trickling filters and conventional activated sludge. This is despite MBRs achieving lower effluent suspended solids and effluent COD than the other two processes.

5. It is hypothesized that the higher SRT (sludge age) of MBRs results in the production of organic molecules able to chelate copper and zinc (and potentially other heavy metals) retaining them in solution and thus preventing their removal.

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APPENDIX B OCCURRENCE AND FATE OF PHARMACEUTICAL AND PERSONAL CARE PRODUCTS IN A SEWAGE TREATMENT WORKS

Rubén Reif[1], Ana Santos[2], Simon J. Judd[2], Juan M. Lema[1] and Francisco Omil[1]

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[1]Department of Chemical Engineering, Group of Environmental Engineering and Bioprocesses, University of Santiago de Compostela, Santiago de Compostela, Spain
[2]Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK

Abstract

The occurrence and fate of eight Pharmaceutical and Personal Care Products (PPCPs) during sewage treatment has been studied in a pilot-scale treatment plant comprising a primary settler (2.85 m^3), an aeration tank (1.845 m^3) and a secondary clarifier (0.5 m^3), placed on site at a wastewater treatment works in the north west of the UK. It was fed both with raw sewage and the return liquor produced after sludge centrifugation, thus representing the most common configuration for a municipal sewage treatment plant based on the activated sludge process. Samples were taken at six different locations, including the return liquor stream, and analysed for musk fragrances and pharmaceutically active compounds belonging to various therapeutic groups such as anti-inflammatory drugs, tranquillisers and antiepileptics. Mass balances were conducted for those PPCPs that were quantifiable.

The fate of the PPCPs was found to differ according to their physical-chemical characteristics. Anti-inflammatories underwent degradation process and were almost completely removed from sewage during the biological treatment step. Musk fragrances were only partially removed, through adsorption onto the primary suspended solids and the biomass in the aerobic process, due to their strong lipophilic characteristics. Results of this study provide increasing evidence that the partial removal of these substances through the sewage

treatment process contribute to environmental occurrence of PPCPs. Consequently, existing WwTWs should be upgraded in order to attenuate the release of these substances into the aquatic environment.

1. Introduction

Over the last decade, the occurrence of trace amounts of pharmaceutical products and other chemical ingredients from cosmetics in lakes, rivers and even tap water has become of increasing concern (Ashton *et al.*, 2004; Heberer, 2002; Ternes, 1998). These chemicals are often referred as Pharmaceutical and Personal Care Products (PPCPs) and are used in large quantities globally. Only in the last 10 years have analytical methods become sufficiently sensitive to detect and quantify PPCPs at the low concentrations at which they arise (ppb or ppt level). Since then, a few chronic ecotoxicological effects on organisms have been reported. A well known example is the dramatic decrease of vulture species populations in India, caused by traces of the anti-inflammatory drug diclofenac which is present on carrion (Oaks *et al.*, 2004). This has led to the supposition that similar effects might be occurring in surface waters, where aquatic organisms are continuously exposed to complex mixtures of micropollutants and their metabolites. However, there remains a paucity of available information regarding the potential impacts of PPCPs on the aquatic environment at environmentally relevant concentrations. Consequently, the general knowledge about PPCPs fate has gradually improved. It is now recognised that most of these compounds are released into the environment through different pathways. Most relevant are excretions via urine or faeces into the sewage system of unmetabolized fractions of drugs. The fate of these chemicals at an WwTW depends on their individual physical-chemical properties and biodegradability (Suarez *et al.*, 2008). Presently, recalcitrant PPCPs are released into surface water and are not significantly removed by a classical WwTW (Heberer, 2002).

Most of the research on this field has been carried out during normal operation of full-scale WwTWs considering only the liquid phase of both raw influent and final effluent to estimate overall removal rates without consideration of the influence of the different removal mechanisms. A few studies considered different sampling points along the studied WwTW, involving intensive sampling campaigns to generate mass balances (Carballa *et al.*, 2004), but the size of

these locations and the daily variations of incoming crude sewage flow makes the generation of consistent results challenging. Pilot or lab scale studies in better controlled conditions, working with synthetic sewage where micropollutants are spiked, have also been performed (Joss *et al.*, 2006), improving the general knowledge about biodegradability of these substances by estimating their biodegradation constants (k_{biol}).

Whilst providing more precise data, lab-based studies are not necessarily representative of processes operated at larger scale. Moreover, the use of synthetic media in some cases may not be representative of behaviour of these substances in sewage treatment since actual full-scale works would also be expected to receive both PPCP parent compounds and their metabolites and conjugates, the fate of which may differ from the parent compounds. Additionally, many works have been carried out using significantly different values of operational parameters such as Hydraulic Retention Time (HRT) and Sludge Retention Time (SRT) which are known to influence the removal capacity of the treatment processes, making difficult to draw general conclusions when comparing different research works. Therefore, many of the gathered results are subjected to a high uncertainty, as can be easily observed comparing removal efficiencies from different works. For example, ibuprofen (IBP) and naproxen (NPX) are considered polar substances that easily undergo biological transformation, but reported removal rates ranges between 60-90% and 40-90% respectively (Ternes, 1998; Carballa *et al.*, 2004; Nakada *et al.*, 2006; Gomez *et al.*, 2007; Stumpf *et al.,* 1999; Zwiener *et al.*, 2000). Diclofenac (DCF) available data is even more dispersed and contradictory since reported removal rates ranged from 0 up to 75% (Ternes, 1998; Gomez *et al.*, 2007; Stumpf *et al.,* 1999; Zwiener *et al.*, 2000; Clara *et al.*, 2005). In the case of musk fragrances, they are substances characterized by a high lipophillicity which enables their removal from the liquid phase following a sorption mechanism onto either suspended solids or biological sludge. However, a further degradation or volatilisation might be achieved due to their retention inside the aeration tank but there is not a general consensus about this possibility and again, reported removal rates are affected by a high variability

(39-90% for galaxolide (HHCB) and 53-96% for tonalide (AHTN) (Kanda *et al.*, 2003; Bester, 2004; Kupper *et al.*, 2006). It is thus important to confirm previous research and to extend understanding of the processes involved in PPCPs removal along the different treatment steps in WwTWs. Consequently, this work was carried out using similar conditions and operational parameters to the typically set on conventional sewage works, considering every stream entering or leaving the different units involved in the sewage treatment process. Simultaneous treatment of the return liquor produced after sludge centrifugation, also known as sludge reject water, is of particular interest since nowadays increasingly stricter environmental legislation is requiring that many existing WwTWs improve their final effluent quality incorporating technologies able to cope with the simultaneous elimination of organic matter and nutrients, mainly nitrogen and phosphorus. These streams are characterized by high ammonia content and therefore a low COD/N ratio and its treatment might mean a potential improvement for WwTWs since reject waters from sludge digestion might contain around 10-30% of the nitrogen load entering to the treatment plant. Examples of typical sludge reject water composition can be found at Ghyoot *et al.,* (1999) and Wett *et al.,* (1998). However, the composition of such streams in terms of micropollutants and their hypothetical influence in the final effluent quality is usually missed. This work aims to provide more extensive knowledge on the occurrence and fate of PPCPs in sewage treatment processes, and in particular biological treatment, primary and secondary clarification, under strictly controlled conditions by means of a fully instrumented pilot plant operating at the premises of a full-scale WwTW treating raw sewage and a stream of the liquor produced after primary and excess humus sludge treatment, recycled into the aeration tanks and which was considered as a relevant sampling point due to its possibly high PPCPs content.

B.1 Experimental

B.1.1 Pilot-scale activated sludge plant

A diagram of the pilot plant used in this work is shown in Figure Appendix B.1.

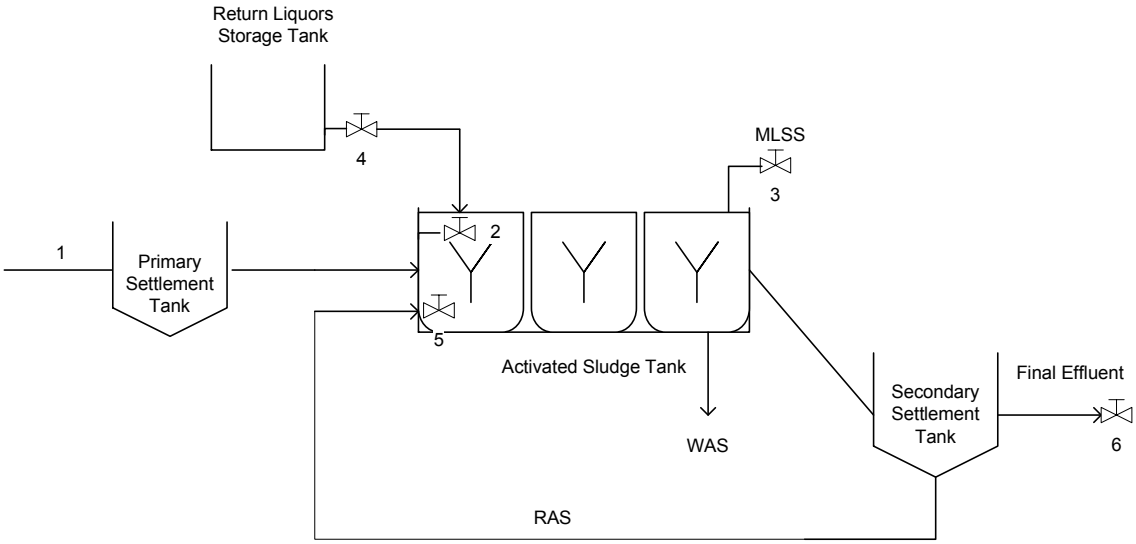

Figure Appendix B.1 Flow sheet of the pilot plant and considered sampling points

The activated sludge tank received both settled sewage and the return liquor which were brought in to the plant weekly from the on-site works centrifuge. The composition of the sludge before centrifugation was 59% of primary sludge, 23.4% of secondary sludge and 17% of sludge from the intermediate settlement tanks. To assist centrifugation, liquid polymer (Allied Colloids) was added to the sludge.

In order to operate the biological unit with a HRT of 6 h, the flow of crude sewage into the primary clarifier was maintained at around 300 l h^{-1}, return liquor stream was fed at 9 l h^{-1} and RAS rate was set at 1.

Throughout the sampling campaign, samples for PPCPs analysis were collected twice a day on each one of the six sampling locations, during two alternate days. Sampling points were the crude sewage, settled sewage, mixed

liquor suspended solids (MLSS) supernatant, return activated sludge (RAS), final effluent and return liquor. Routine physical-chemical analysis was carried out on a daily basis to assess the performance of the pilot plant with respect to aerobic carbonaceous removal and nitrification. These analyses include total and soluble Biochemical Oxygen Demand (BOD and sBOD), total and soluble Chemical Oxygen Demand (COD and sCOD), Total Suspended Solid (TSS) and ammonia. On-site test facilities were available to carry out operational testing such as conductivity, pH and dissolved oxygen for plant monitoring purposes.

B.2 Analytical methods

Total suspended solids (TSS) were determined according to standard methods (HMSO, 1980). Total and soluble COD and ammonia (NH_4^+) were determined using a Spectroquant Cell Test and measured on a Nova 60 model spectrophotometer (Merck, West Drayton, UK). Total and soluble BOD were determined according to standard methods (HMSO, 1988). Conductivity and pH were measured using a Jenway 3540 pH & Conductivity Meter (Jenway, Dunmow, UK) according to standard methods (HMSO, 1978).

Substances considered in this work were galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI), ibuprofen (IBP), naproxen (NPX), diclofenac (DCF), carbamazepine (CBZ) and diazepam (DZP). Sample treatment for PPCPs analysis consisted of a pre-filtration step through glass-fibre filters (APFC04700 or AP4004705, Millipore) immediately after sample collection, followed by filtration through nitrate cellulose membrane filters and addition of sodium diazide (Sigma-Aldrich, UK) as biocide, in order to avoid further biological degradation. PPCPs content was determined after solid-phase extraction (SPE) of 100 ml pre-treated samples for sewage (crude or settled) and return liquor, or 250 ml samples for MLSS or RAS supernatant and final effluent samples, using 60 mg OASIS HLB cartridges (Waters, Milford, MA, USA). Cartridges were eluted with 3 ml of ethyl acetate. SPE extract was divided in two fractions for the

direct determination of the soluble content of carbamazepine, diazepam and fragrances. The second fraction was used for the determination of anti-inflammatory drugs following silylation. GC/MS (Varian Saturn 2100 T) was used to determine the concentration of the investigated compounds in the SPE extract. Every sample was analyzed by duplicate in the GC/MS and the results were averaged. More detailed information about the analysis of the soluble content of anti-inflammatory compounds, CBZ, DZP and musk fragrances can be found at Rodríguez *et al.*, (2003).

B.3 Mass balances calculations

Prior to determining mass balances, PPCPs concentrations sorbed onto sludge were estimated using only solid-water distribution coefficients from the literature (K_d in l kg^{-1}) (Table Appendix B.3). This parameter, defined as the ratio between the concentration in the solid and liquid phases at equilibrium conditions, can reasonably predict PPCPs sorption in WwTW processes (Ternes *et al.*, 2004). Due to the high variability of reported distribution coefficients and considering that these parameters might be matrix dependant, a selection criteria was followed: Chosen K_d values were always experimentally determined, avoiding the selection of coefficients estimated with theoretical calculations. Table Appendix B.1 shows the parameters that were chosen, for primary or secondary sludge and return liquor, and other physical-chemical properties

Table Appendix B.1 PPCPs detected and their physical-chemical properties (Suarez *et al.*, 2008)

PPCP	Therapeutic class	CAS	pKa	s	H	K_{biol}	log K_d		
							Primary	Secondary	Return Liquor
Ibuprofen (IBP)	Anti-inflammatory	15687-21-1	4.9-5.2	21	$6.1x10^{-6}$	9-35	<1.3	0.9	1.1
Naproxen (NPX)		22204-53-1	4.2	16	$1.4x10^{-8}$	0.4-1.9	1.1	1.1	1.1
Diclofenac (DCF)		15307-86-5	4.1-4.2	2.4	$1.9x10^{-10}$	<0.1	2.7	1.2	1.95
Galaxolide (HHCB)	Fragrances	1222-05-5	-	1.8	$5.4x10^{-3}$	<0.03	3.7	3.3	3.5
Tonalide (AHTN)		1506-02-1	-	1.2	$5.1x10^{-3}$	<0.02	3.7	3.4	3.55

s: solubility in water in mg l^{-1}; H: Henry´s law constant; K_d: sludge-water distribution coefficient in l kg^{-1} SS (Ternes *et al.,* 2004; Urase and Kikuta (2005); K_{biol}: pseudo first-order degradation constant in l g^{-1} SS d^{-1} (Joss *et al.,* 2006)

In carrying out mass balances, some assumptions had to be made:

- Since no data were found in the literature, PPCPs concentration sorbed onto return liquor was estimated using a mean K_d value calculated from the ones reported for both primary and secondary sludge.
- The primary K_d value for NPX was assumed to be the same as that for secondary.
- Since the IBP, DCF and AHTN concentrations measured in certain samples were below its detection or quantification limit, mass balances which depended on these samples were calculated using these limit values.

Total mass fluxes for PPCPs load on each stream (Figure Appendix B.2) were calculated according to the next expression:

$$m = Q_{in}(S + X) \quad \textbf{(B.1)}$$

Where m is the mass flux of PPCP (µg PPCP d^{-1}) entering or leaving a specific unit of the WwTW, Q is the sum of incoming flows (l d^{-1}), S is the PPCP concentration in the liquid phase (µg PPCP l^{-1}) and X (µg PPCP l^{-1}) is the amount of PPCP estimated to be sorbed onto the sludge phase.

B.4 Results and discussion

B.4.1 Conventional parameters

The pilot-plant was operated in similar conditions to correctly operated full-scale WwTWs. Table Appendix B.2 shows the values for conventional parameters measured in different sampling points and general sludge quality parameters during the sampling week.

Table Appendix B.2 Characterization of conventional parameters in the sampling points

Stream	BOD, mg l^{-1}		sBOD, mg l^{-1}		COD, mg l^{-1}		sCOD, mg l^{-1}		NH_4^+, mg l^{-1}		TSS, mg l^{-1}	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Settled Sewage	111.5	34.8	55.8	13.9	299.2	44.1	132.8	24.7	24.0	3.7	83.4	27.8
Final Effluent	10.5	12.9	2.7	0.9	56.0	46.7	25.9	4.9	0.4	0.0	32.0	29.4
RAS	-	-	-	-	-	-	-	-	-	-	9818.0	1643.1
Aeration Tank	1922.2	683.3	47.4	21.2	6499.0	780.5	59.5	35.1	-	-	4870.0	567.1

	T, ºC	pH	DO, mg l^{-1}	ORP, mV	SVI, ml g^{-1}
Aeration Tank	16.60	7.20	6.00	66.40	101.30
Secondary Settler	16.60	7.10	2.20	16.40	-

Eight weeks after seeding with sludge from the on-site activated sludge bioreactor, stable MLSS concentration and acclimatisation conditions (>96% nitrification) were achieved and the sampling campaign was carried out. Dissolved oxygen content was always kept high enough (~6 mg l^{-1}) to guarantee the development of a stable population of heterothropic and nitrifying bacteria. Temperature and pH were not controlled, but their values (16ºC and 7 respectively) were representative of the normal situation in full-scale WwTWs. The Sludge Volumetric Index (SVI) was in the common range (50-150 ml g^{-1}) for these systems. Therefore, the concentration of solids in the final effluent was low (<76 mg l^{-1}), which helped to maintain a SRT above 150 days (optimum for the development of slowly growing bacteria such as nitrifiers). Carbon removal and nitrification occurred efficiently since COD (total and soluble) and ammonia overall removals were 80 and 98% respectively.

B.4.2 Occurrence of selected PPCPs in the pilot plant.

Table Appendix B.3 displays average concentrations measured for PPCPs detected during the two sampling days in the different locations, together with the detection/quantification limits and the removal rates from the liquid phase.

The musk fragrance ADBI was not found at any sample and, on the contrary, HHCB and AHTN were found at substantial levels (2.0 and 0.9 µg l^{-1} respectively). These two fragrances comprise about 95% of the EU market and 90% of the USA market for all polycyclic musks (HERA, 2004). The ratio between the detected levels of HHCB and AHTN (2-3) is slightly lower compared with many previous works. Reiner *et al.*, (2007) compared concentrations detected in two different WwTWs for both musk fragrances and found influent concentrations of HHCB 4.5 to 6 times higher than AHTN. However, those results and the ones presented on this work are indicative of the greater production and use of HHCB compared with AHTN.

Table Appendix B.3 Concentrations of PPCPs (µg l^{-1}) detected along the different units of the pilot plant, removal rates and standard deviations

Sampling Location	IBP	*n*	NPX	*n*	DCF	*n*	HHCB	*n*	AHTN	*n*
Crude Sewage	7.5	3	3.0	3	<0.1	3	1.59	3	0.70	2
SD	0.67		0.42		n.a		0.34		0.20	
Primary Effluent	7.5	8	3.0	8	<0.1	8	1.54	8	0.70	4
SD	1.4		0.5		n.a		0.36		0.20	
Return Liquor	4.6	4	1.7	4	<0.1	4	0.69	4	<0.023	4
SD	0.9		0.3		n.a		0.29		n.a	
MLSS Supernatant	<0.08	3	0.2	1	1.2	3	1.06	3	0.37	3
SD	n.a		n.a.		0.309		0.08		0.03	
RAS	<0.08	3	0.2	1	1.2	3	0.96	3	0.36	3
SD	n.a		n.a.		0.43		0.05		0.01	
Final Effluent	0.2	2	0.2	3	1.1	4	1.07	4	0.37	4
SD	0.08		0.01		0.33		0.06		0.01	
Removal Rate, %	98		93		0-45		33		48	
LOD	0.03		0.03		0.10		0.02		0.02	
LOQ	0.08		0.08		0.30		0.07		0.07	

(LOD: detection limit; LOQ: quantification limit; n: number of samples; n.a.: not available)

Similarly to ADBI, the tranquilliser DZP was not found at any sample. This substance is not normally detected in WwTWs, and very few authors managed to detect concentrations even in the low ng l^{-1} range (Castiglioni *et al.*, 2006). CBZ was found in some locations during the first day of sampling, but the levels detected were always below the quantification limit of the analytical method (1.4 µg l^{-1}), which is particularly high for this substance. Considering that typically reported concentrations for CBZ are similar or below this value (Clara *et al.*, 2004), this result might be expected. However, it is interesting to mention that the detected levels were always higher in the final effluent, MLSS and RAS compared with the crude and settled sewage streams, leading to apparent negative removal rates. This behaviour through the sewage treatment process has been reported for CBZ and other substances such as antibiotics or β-blockers (Lishman *et al.*, 2006). Pharmaceuticals enter WwTWs as either the

original compound or as one of its metabolites, for example, glucoronide conjugates which remains undetected in the wastewater matrix. If these products are transformed during the treatment process to liberate the original compound, calculated removal rates might be underestimated. Considering that CBZ is considered a persistent substance (Clara *et al.*, 2004), in case its conjugates are transformed back to the parent compound during the biological treatment step, it would not undergo a further degradation process leading to higher outlet concentrations.

IBP was detected at the highest levels in sewage samples compared to the rest of the targeted pharmaceuticals, which is consistent with consumption rates reported for many EU countries (Carballa *et al.*, 2008). On the other hand, DCF concentrations were below detection limit in the sewage (crude and settled) and return liquor samples whereas it was correctly quantified in the MLSS, RAS and final effluent samples. Consequently, increased effluent concentrations were found leading to estimate negative removal efficiencies. This trend has already been observed by other authors. Lishman *et al.* (2006) pointed out that some deconjugation of acidic drugs within the collection and treatment system of WwTWs might be expected and also mentioned that mention that, during the analytical process, extraction recoveries were lower for raw influent because the elution of co-extractives from the SPE cartridges could have caused the derivatization efficiency to drop. Moreover, Reddersen *et al.,* (2003) reported analytical issues for DCF measures based on acidic (pH=2) solid-phase extraction of matrix-prone samples such as WwTW influents. As a consequence, it was not feasible to calculate accurately its removal efficiency and to estimate mass balances. In this work, DCF was found to have the second highest mean concentration in the final effluent samples. Ashton *et al.,* (2004) investigated the occurrence of several pharmaceuticals, including IBP and DCF, in several WwTW effluents and surface waters from the UK. The range of DCF concentrations detected in the final effluent of the pilot plant (0.8-1.4 μg l^{-1}) is consistent with this previous research in WwTWs from the UK. On the other hand, IBP concentrations, which ranged from 0.1-0.3 μg l^{-1}, were significantly lower than the ones reported by Ashton *et al.,* (2004). Comparing

with treated wastewaters of different countries such as France, Greece, Italy, Sweden or Canada (Andreozzi *et al.*, 2003; Metcalfe *et al.*, 2004), strong variations are observed between median and maximum IBP concentrations among the different countries. Whereas prescription rates and usage profiles may differ strongly from country to country, different factors (operational parameters, technology of the studied WwTWs, analytical methodologies and sampling protocols) are indeed decisive in the data variability, confirming the necessity of carrying out works in this field with better controlled conditions and following similar operational criteria.

Regarding the removal efficiencies from the liquid phase, IBP (98%) and NPX (93%) were almost completely eliminated. In the case of DCF, typically reported concentrations in raw sewage are usually in the range of 0.5-2 μg l^{-1} (Alder *et al.*, 2006; Rosal *et al.*, 2010). Comparing these reported levels with the ones measured in the effluent, it might be considered that the removal of DCF was low or negligible. However, the lack of DCF concentrations data in the sewage stream makes difficult to draw definite conclusions regarding the fate of this substance. Musk fragrances removal from the liquid phase was from moderate to intermediate (30-50%). These substances have high solid-water distribution coefficients (Table Appendix B.1) and consequently, they tend to be attached onto the particulate phase, representing a good example of the importance of considering both liquid and solid phase in order to determine overall removal efficiencies, as will be discussed in the following section.

B.5 Mass balances

The calculation of mass balances in every unit permits to identify the removal mechanisms involved in each PPCP removal along sewage treatment and to estimate overall removal efficiencies for each compound. Main removal mechanisms are biodegradation, sorption and volatilization (Suarez *et al.*, 2008). The latter is influenced by the Henry´s coefficient, only relevant for ADBI, which was not detected. In the remaining compounds, volatilization only

accounts for less than 2% of removal (Joss *et al.*, 2006). Therefore, volatilization will not be considered in this work. Figure Appendix B.2 shows calculated mass balances considering both liquid and solid phase, which were calculated with the average values from the two sampling days (Table Appendix B.2), and Figure Appendix B.3 shows the overall removal efficiencies.

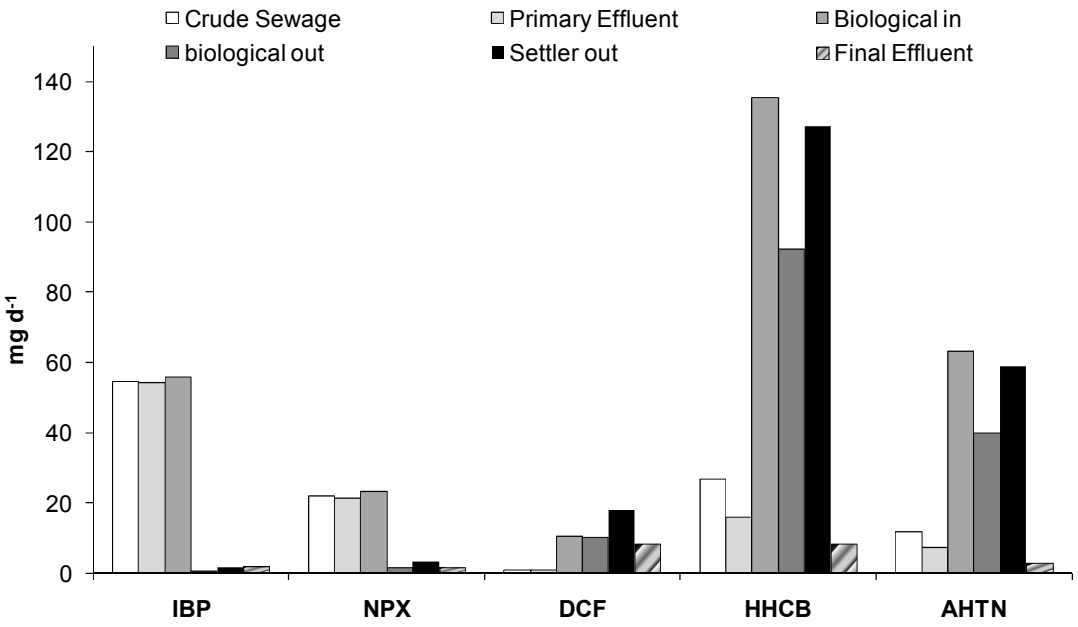

Figure Appendix B.2 Mean mass balances of PPCPs calculated along the different units of the studied WwTW

Crude Sewage represents the load of PPCPs in the crude sewage stream. Primary effluent load is calculated based on the settled sewage stream. RAS, settled sewage and return liquor are incorporated into the calculation of the activated sludge tank influent stream (Biological in), MLSS supernatant is the only stream considered for the activated sludge tank effluent (Biological out), which match up with the incoming load into the secondary settler (not shown). The load following secondary clarification (Settler out) is calculated from the final effluent and RAS samples and the Final Effluent stream was calculated considering only the values from the final effluent samples.

Ibuprofen incoming load (54.6 mg d^{-1}) was the highest of all PPCPs and its elimination took place mainly along biological treatment (98%), confirming the biological degradation as its main removal mechanism. No differences were observed when comparing its removal rate from the liquid phase with the overall removal calculated after incorporating solid-phase data (Figure Appendix B.3), which permits to confirm that IBP is a polar substance with no tendency to be sorpted onto solids. A similar behaviour was observed for NPX in terms of overall removal and sorption behaviour. In despite of an incoming load of 21.9 mg d^{-1}, half of the amount of IBP, NPX removal rate was slightly lower (93%). According to Joss *et al.,* (2006) the biological degradation constant of this pharmaceutical is moderate (1-1.9 l g^{-1} SS d^{-1}), one order of magnitude below the IBP constant (21-35 l g^{-1} SS d^{-1}). Therefore, longer HRTs or higher MLSS concentrations are necessary for achieving significant NPX removals. In this work, the established HRT of 6 h might be low, but the MLSS concentration (~5 g l^{-1}) was high enough to remove this substance in a significant rate.

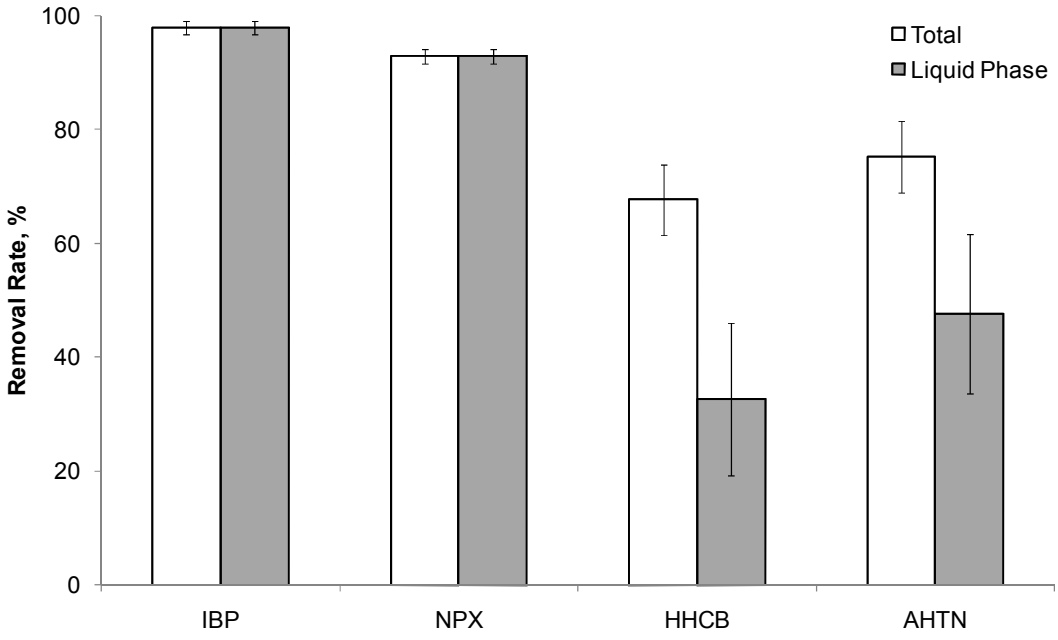

Figure Appendix B.3 Global removal efficiencies calculated for PPCPs

Diclofenac mass flow load in the final effluent stream was considerably higher (8.4 mg d^{-1}) in comparison with IBP and NPX. Considering previously mentioned occurrence data, it can be assumed that its incoming load was lower compared to those of IBP and NPX and therefore its removal might be estimated as low or negligible. This finding is also confirmed by its low degradation constant and distribution coefficient (Table Appendix B.3). Considering that MLSS and SRT were high enough, the only possibility to enhance the DCF removal along biological treatment might be to establish considerably longer HRTs, which indeed might affect the overall output of the WwTW, mainly in economic terms.

For both polycyclic musk fragrances, a certain degree of removal was achieved after primary settling. This behaviour might be due to their strong lipophillic character and indicates that removal following a sorption mechanism occurs along every stream which contains suspended solids. A marked increase in HHCB and AHTN incoming loads into the aeration tank was observed because of the influence of the return liquor and particularly the RAS stream. As a difference with the pharmaceuticals, a significant reduction of the fragrances load was observed comparing the biological out and final effluent streams, due to the solids separation after secondary settling. After this final step, the total removal rates achieved in the pilot plant were 68% for HHCB and 75% for AHTN (Figure Appendix B.3), significantly higher compared with the liquid phase data. A certain degree of biodegradation might also be achieved in despite of the low K_{biol} values reported for musk fragrances (Table Appendix B.3), as a consequence of longer retention times inside the reactor due to their association with solids. This supposition is based considering works which detected HHCB-lactone, product of HHCB oxidation, in treated effluents (Reiner *et al.*, 2007). Nevertheless, the calculated mass balances of this work indicate that the key removal mechanism for fragrances is the sorption onto the particulate phase, primarily during the biological treatment step. Despite the degree of removal achieved, the loads in the final effluent for HHCB and AHTN were 8.3 and 2.9 mg d^{-1} respectively, which are considerably higher than the ones measured for IBP and NPX (1.2 and 1.6 mg d^{-1} respectively) and similar to

DCF load, in the case of HHCB. Considering that the average flow rate of the full-scale WwTW where this research was conducted is 54,000 m^3 d^{-1}, the estimated release of HHCB or DCF in the discharged liquid stream would be of 1.5 kg *per* day. In order to draw additional conclusions about the strategies that should be followed in order to attenuate the release of PPCPs into the aquatic environment, a direct comparison among removal rates reported in this work and previous research carried out by Carballa *et al.,* (2004) in a WwTW located in north west Spain can be done, since most of the studied substances and analytical methodologies were similar. Interestingly, there are significant differences: IBP and NPX eliminations from the liquid phase were somewhat lower and fragrances removal rates were particularly high compared with our work. The elimination of HHCB and AHTN along pre-treatment and primary treatment steps accounted for half of their overall removal along the WwTW whereas in the present work most of the removal took place mainly along secondary treatment. As a feasible explanation, the full-scale WwTW incorporated an additional pre-treatment step (based on screenings and grit-fat removal) and more efficient primary settlers which enabled to work with longer HRTs along primary treatment. On the other hand, the removal rates of IBP and NPX were considerably higher in our work (65 and 50% *vs* 93 and 99% respectively). In this case, the main difference between both biological treatments is based on the SRT, considered an influencing parameter in terms of PPCPs removal (Clara *et al.*, 2005). In the full-scale WwTW, no ammonia removal was achieved since a low SRTs of 1-3 days was established, whereas the correct design and operation of the studied pilot plant enabled to work with extended SRTs of 150 days. This operational strategy permitted to enhance the overall treatment quality, improving significantly the removal rates of IBP and NPX. The results clearly show the necessity to enhance the sewage treatment quality in order to attenuate the release of micropollutants into the aquatic environment.

B.6 Return liquor treatment

Table Appendix B.4 shows conventional parameters analysis performed during the sampling week on the return liquor which were directly fed into the aeration tank. Comparing with data reported for reject water from sludge digestion (Ghyoot *et al.*, 1999; Wett *et al.*, 1998), nitrogen concentrations were lower but, on the contrary, COD (total and soluble) and TSS values were significantly higher.

Table Appendix B.4 Conventional analysis of the return liquor in mg l^{-1}

Day	TSS	BOD	sBOD	COD	sCOD	Ammonia
Monday	1110	1540	777	2940	1680	89.8
Tuesday	840	1880	789	3000	1560	88.2
Wednesday	780	1520	458	2950	1540	84.8
Thursday	790	1250	582	2810	1800	92
Friday	1060	1020	581	3010	1820	86.8
Mean	*916.00*	*1442.00*	*637.40*	*2942*	*1680.00*	*88.32*
SD	*156.94*	*325.00*	*142.20*	*79.81*	*130.38*	*2.76*

With respect to the treated settled sewage stream, considerably higher values were detected for the measured parameters in the return liquor. In despite of this, the overall treatment capacity of the pilot plant was always excellent in terms of COD (total and soluble) and ammonia removal with no apparent impact on its normal operation, which confirms the benefits of treating this kind of streams in the conventional biological treatment. Regarding the studied PPCPs, their concentrations in the return liquor were roughly the half of the measured in the crude sewage stream (Table Appendix B.2) with the exception of the musk fragrance AHTN, which concentration was below detection limit. Therefore, the detected levels confirm that a biological treatment of the return liquor is beneficial also in terms of PPCPs removal and its influence on the overall treatment can be considered negligible, considering that the flow rate of this

stream was significantly lower compared with the main stream of settled sewage coming into the aeration tank.

B.7 Conclusions

The pilot plant described in this work, based on the activated sludge system, has proven to be very effective for a combined treatment of both urban sewage and return liquor from sludge centrifugation. Moreover, COD (total and soluble) removal was always high, a nitrification rate up to 96% was easily achieved and no adverse effects were observed after treating the return liquor stream. Eight different PPCPs were analyzed in sewage samples and along the inflow/outflow of the different units of the pilot plant. Only AHTN and DZP remained below the detection limit, and CBZ was found in a few discrete samples. After estimating amounts of PPCPs sorbed onto solids, complete mass balances were calculated. The analysis of PPCPs behaviour along the different units helped to ascertain the two main removal mechanisms involved. Anti-inflammatory drugs were mainly removed inside the activated sludge tank, most probably by biological degradation, whereas musk fragrances removal occurred by sorption onto solids and arose in the primary or secondary sludge. PPCPs levels in the return liquor from sludge centrifugation were approximately the half of the crude sewage, which confirms the benefits of treating such streams since no apparent influence on the overall removal of conventional parameters or PPCPs was observed.

In general, results observed in this work corroborate some of the previously reported after intensive sampling in full-scale treatment plants (Carballa *et al.*, 2004; Artola-Garicano *et al.*, 2003). Almost complete removal rates were observed for IBP, NPX, and intermediate in the case of HHCB and AHTN. DCF concentration in the final effluent was the highest of this work (up to 1.1 μg l^{-1}), which might be indicative of a low or negligible removal potential. However, this substance could not be detected in sewage samples and therefore, it was not

possible to confirm this trend with the available data. The calculated mass balances for the outflow load permitted to estimate a release of PPCPs in the range of 0.3-1.5 kg *per* day, depending on the substance considered. This estimation confirms that the development of enhancement strategies in existing plants should be a priority since it might help to attenuate the release of micropollutants in the water cycle, though new treatment and post-treatment technologies such as membrane bioreactors or ozonation are likely to continue to be explored.

Acknowledgements

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APPENDIX C CRITICALITY OF FLUX AND AERATION ON HF SIDESTREAM MEMBRANE BIOREACTOR

Ana Santos and Simon J. Judd

Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK

C.1 Materials and Methods

The hydraulic performance of four sidestream HF membranes module, two with higher pure water permeability (*H1* and *H2*) and two with lower (*L1* and *L2*) (Table Appendix C.1), were tested in parallel with the immersed HF modules tested during Campaigns 4 and 5 (Chapter 9). The MBR pilot plant operated is described in Chapter 9, and sludge and water (influent and effluent) quality determinants monitored according to Chapter 9. Throughout the campaigns the removal of COD and ammonia were always greater than 80% with average influent concentration of 262.1 (±109.7) COD, 25.9 (±13.5) NH_4, 2.61 (±4.06) NO_3 and 7.3 (±0.30) pH. During campaigns 4 and 5, the MLSS was held at 3.3 and 6.9 g l^{-1}, respectively.

Table Appendix C.1 Modules characteristics for the four sidestream membrane modules

Characteristics	*L*1	*L2*	*H*1	*H2*
Membrane chemistry	Proprietary PVDF			
Membrane type	Hollow fibre outside-in operation			
Surface area, m^2	3.00			
Nominal pore size, μm	0.10	0.13	0.15	0.19
Outer diameter, mm	2.34	2.20	2.30	2.20
Inner diameter, mm	1.15	1.15	1.10	1.20
Fibre length, mm	429	961	602	913
Pure water permeability, l m^{-2} h^{-1} bar^{-1}	390	656	1077	1597

C.1.1 Critical flux and aeration

All criticality tests performed on the immersed HF modules were also performed on the sidestream modules using the same criteria (Chapter 8; Chapter 9). The experimental conditions are outlined in Table Appendix C.2.

Prior to each test a chemically-enhanced backflush (CEB) was applied. The modules were first rinsed with clean water at a low aeration rate before being immersed in a 500 mg l^{-1} sodium hypochlorite (NaOCl) solution at low aeration for a minimum of 2 hours.

Table Appendix C.2 Experimental conditions for criticality test

Critical flux, J_c	Value
Filtration flux, l m^{-2} h^{-1}	5-35 (intervals of ~5)
Filtration cycle	9 min on/1 min off (relaxation)
Filtration duration (total), min	20
SAD_m, Nm^3 h^{-1} m^{-2}	Continuous: 0.40[a]
	Intermittent: 0.20
Aeration frequency	Continuous
	Intermittent: 10 sec on/10 sec off
Feed liquid upflow velocity, m h^{-1}	0.025-0.054
Critical aeration, $SAD_{m,crit}$	
Filtration flux, l m^{-2} h^{-1}	Fixed at critical flux previously observed
Filtration cycle	14 min on/1 min off (relaxation)
Filtration duration, min	30
SAD_m, Nm^3 h^{-1} m^{-2}	Continuous: 1 to 0.1 (intervals of 0.2-0.1)
	Intermittent: 0.5 to 0.05 (intervals of 0.06-0.03)
Aeration frequency	Continuous
	Intermittent: 10 sec on/10 sec off
Feed liquid upflow velocity, m h^{-1}	0.025-0.054

a: values typically recommend for sidestream HF modules by manufacturers.

C.1.2 Sludge upflow test

During campaign 4, the impact of upflow velocity was studied on *L1* and *H1* modules by stepping the sludge flow through manual adjustment of the sludge feed ball valve under fixed conditions of flux and SAD_m (Table Appendix C.3). The flux was set at the critical flux value previously recorded and the aeration demand at the least conservative value. Using the same modules, the critical SAD_m step test was performed using sludge pumping and airlift regime (*i.e.* with and without sludge pumping) (Table Appendix C.4).

Table Appendix C.3 Experimental conditions for critical upflow velocity test

Parameter	Value
Filtration flux, l m^{-2} h^{-1}	12 and 17 (*L1* and *H1* respectively)
Filtration cycle	9 min on/1 min off (relaxation)
Filtration duration, min	20
SAD_m, Nm^3 h^{-1} m^{-2}	0.20
Aeration frequency	Continuous: 1 to 0.1 (intervals of 0.2-0.1)
Feed liquid velocity, m h^{-1}	0.00004-0.04 and 0.00009-0.08 (*L1* and *H1* respectively)

Table Appendix C.4 Experimental conditions for SAD_m test sludge airlift regime

Parameter	Value
Filtration flux, l m^{-2} h^{-1}	12 and 17 (*L1* and *H1* respectively)
Filtration cycle	14 min on/1 min off (relaxation)
Filtration duration, min	30
SAD_m, Nm^3 h^{-1} m^{-2}	0.20
Aeration frequency	Continuous: 1 to 0.1 (intervals of 0.2-0.1)
Feed liquid velocity, m h^{-1}	0.025 and 0.043 (*L1* and *H1* respectively)

C.2 Results

C.2.1 Critical flux and aeration test

The critical flux and critical aeration determined for the sidestream HF modules is summarised in Table Appendix C.5. The critical flux found for *L1* and *L2* was 11.9 and 17.7 l m^{-2} h^{-1} under conditions of continuous aeration (Figure Appendix C.1 and Figure Appendix C.2). For intermittent aeration, the corresponding values were 14.7 and 17.1 l m^{-2} h^{-1}. Contrary to results obtained with the other modules, the *L1* module critical flux value obtained for intermittent aeration was higher than that measured for continuous aeration. For the *H1* module the critical flux determined was 16.7 l m^{-2} h^{-1} for continuous aeration conditions and 15.5 l m^{-2} h^{-1} for intermittent (Figure Appendix C.3). These values were higher than the corresponding values of 15.7 and 12.9 l m^{-2} h^{-1} respectively measured for the *H2* module (Figure Appendix C.4).

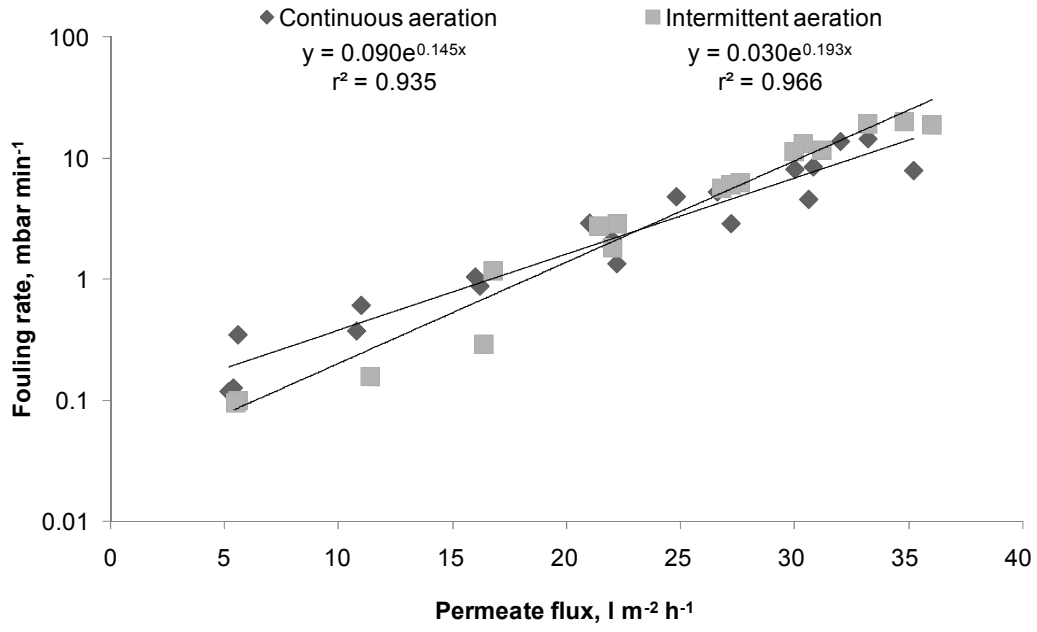

Figure Appendix C.1 Fouling rate *vs* permeate flux for *L1* sidestream module

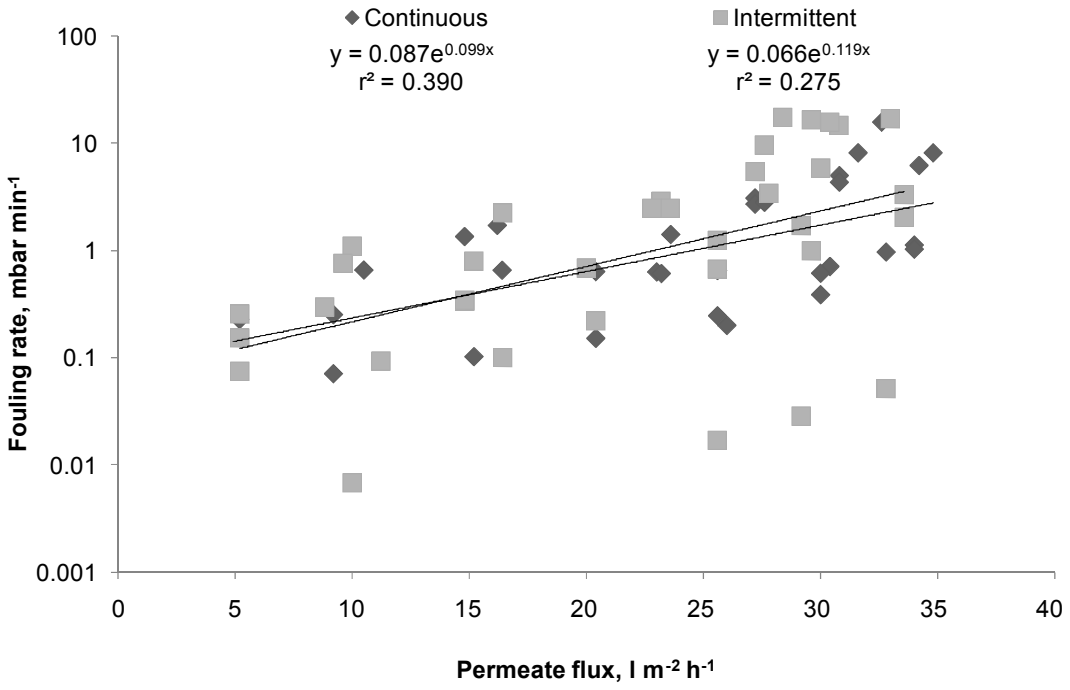

Figure Appendix C.2 Fouling rate *vs* permeate flux for *L2* sidestream module

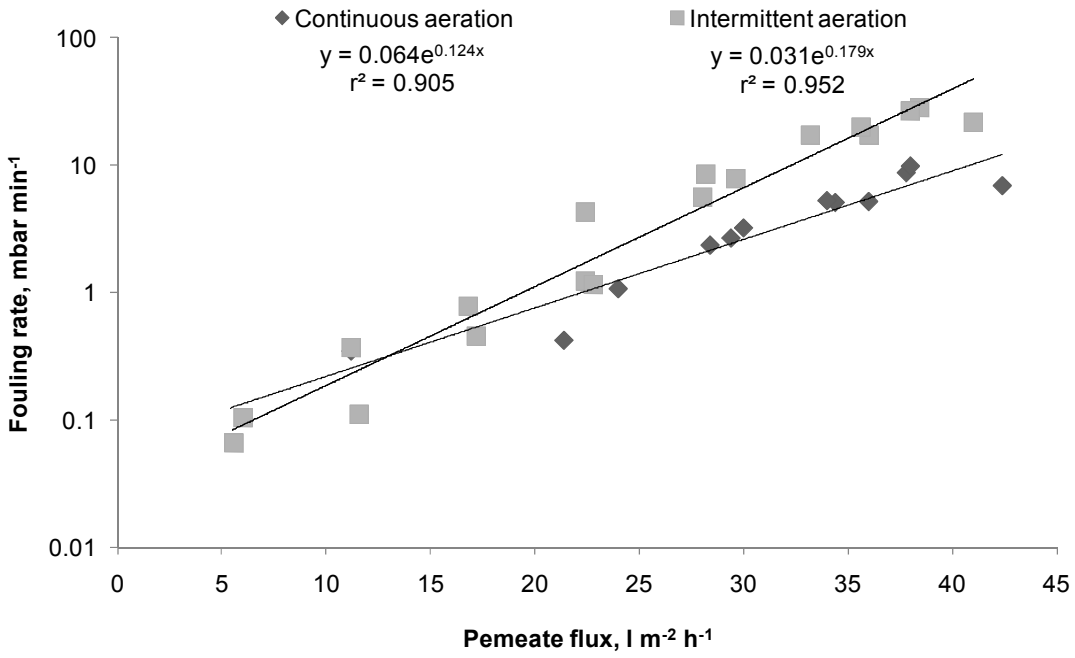

Figure Appendix C.3 Fouling rate *vs* permeate flux for *H1* sidestream module

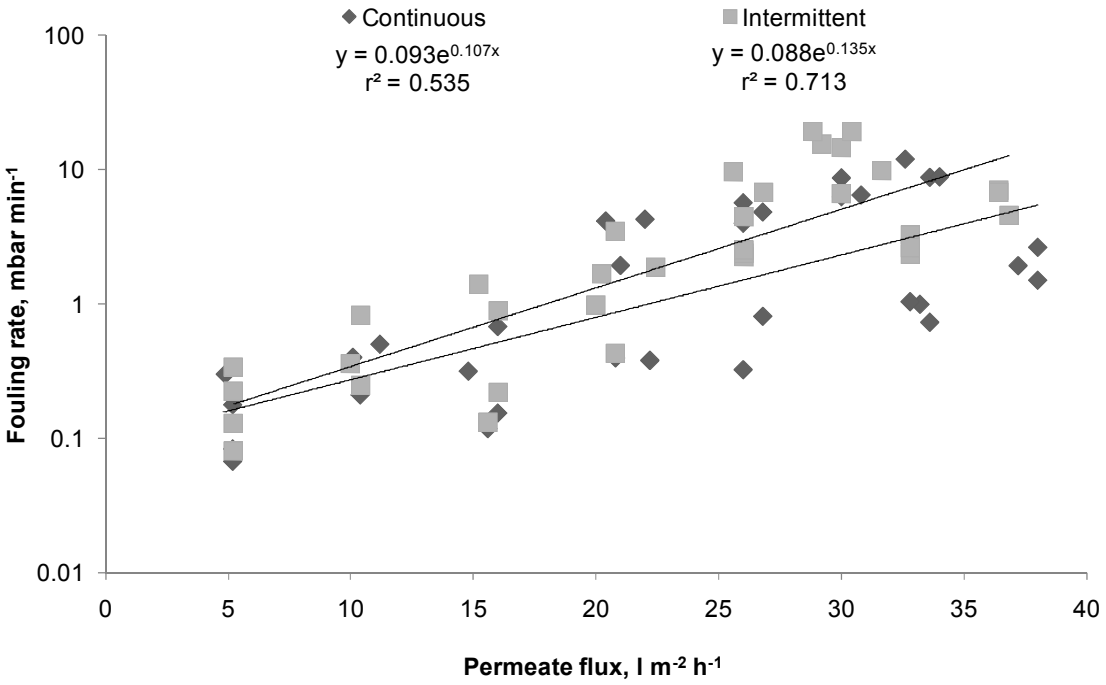

Figure Appendix C.4 Fouling rate *vs* permeate flux for *H2* sidestream module

Different aeration patterns were identified, at the same air flow, between the *L1* and *H1* modules. Figure Appendix C.5 and Figure Appendix C.6 show the pressure transducer outputs from the tests performed. For the *H1* module, larger and vigorous aeration was observed, possibly explaining the high critical flux value obtained for the *H1* module (Figure Appendix C.5; Figure Appendix C.6). Although for the *L2* and *H2* modules the aeration pattern appeared to be more consistent, the data obtained was more scattered (Figure Appendix C.7; Figure Appendix C.8).

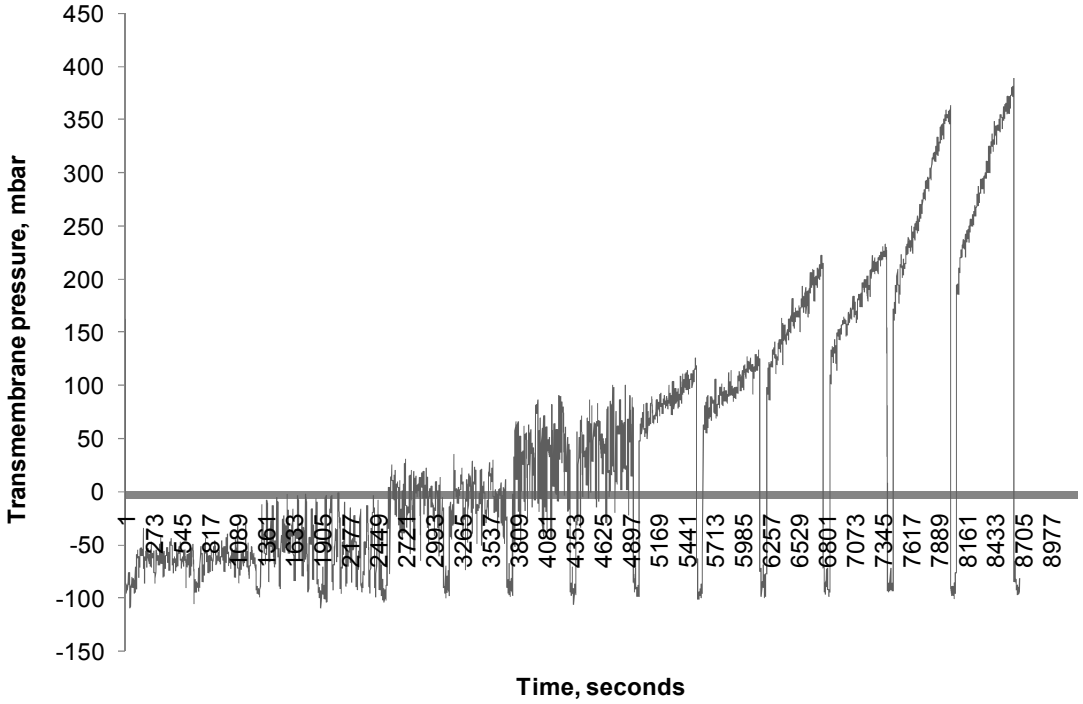

Figure Appendix C.5 Transmembrane pressure *vs* time for *L1* sidestream module

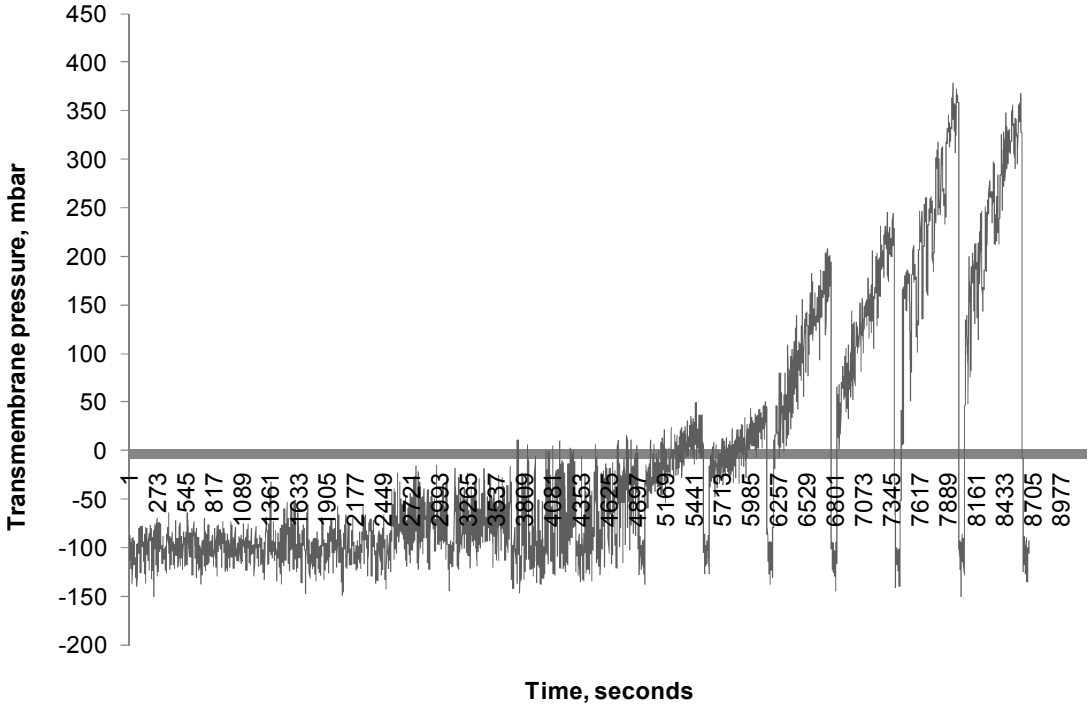

Figure Appendix C.6 Transmembrane pressure *vs* time for *H1* sidestream module

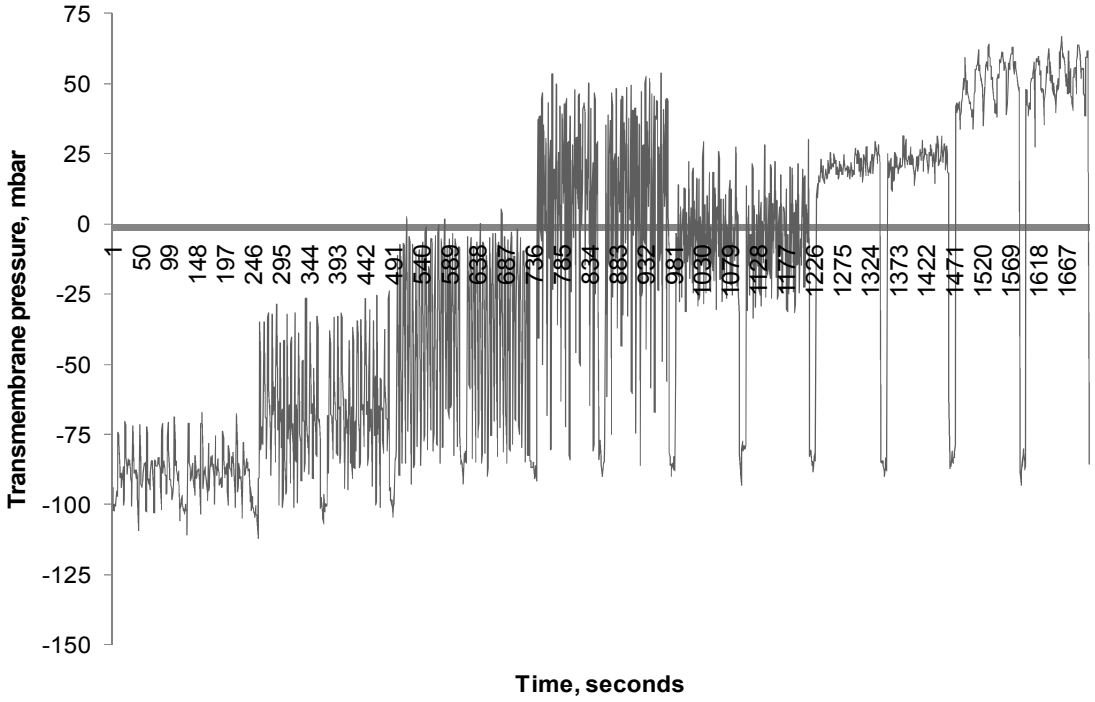

Figure Appendix C.7 Transmembrane pressure *vs* time for *L2* sidestream module

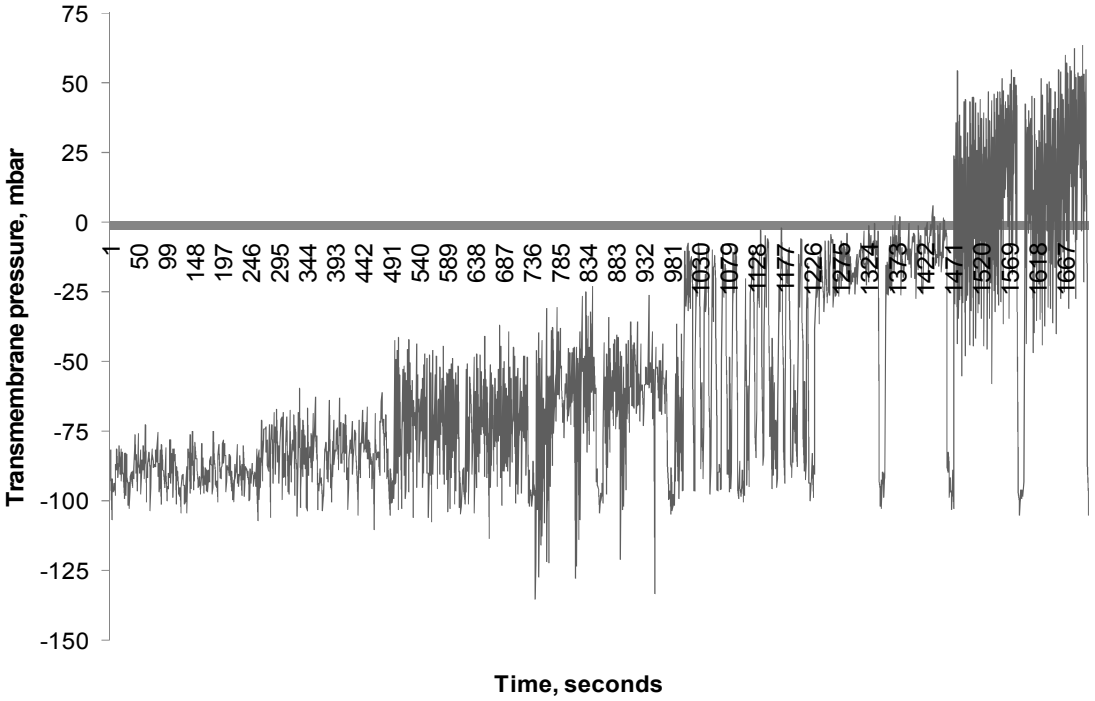

Figure Appendix C.8 Transmembrane pressure *vs* time for *H2* sidestream module

The SAD_m step experiments performed at the measured critical flux (Table Appendix C.5) reveal $SAD_{m,crit}$ values of 0.45 and -0.13 $Nm^3\ m^{-2}\ h^{-1}$ under continuous aeration conditions and 0.13 and 0.70 $Nm^3\ m^{-2}\ h^{-1}$ for intermittent aeration for the *L1* and *L2* modules respectively (Figure Appendix C.9; Figure Appendix C.10). For the *H1* and *H2* module, the recorded $SAD_{m,crit}$ values were respectively 0.28 and 1.03 $Nm^3\ m^{-2}\ h^{-1}$ for continuous aeration and 0.27 and 0.18 $Nm^3\ m^{-2}\ h^{-1}$ for intermittent aeration (Figure Appendix C.11; Figure Appendix C.12). The data are less consistent than those obtained for the critical flux determination.

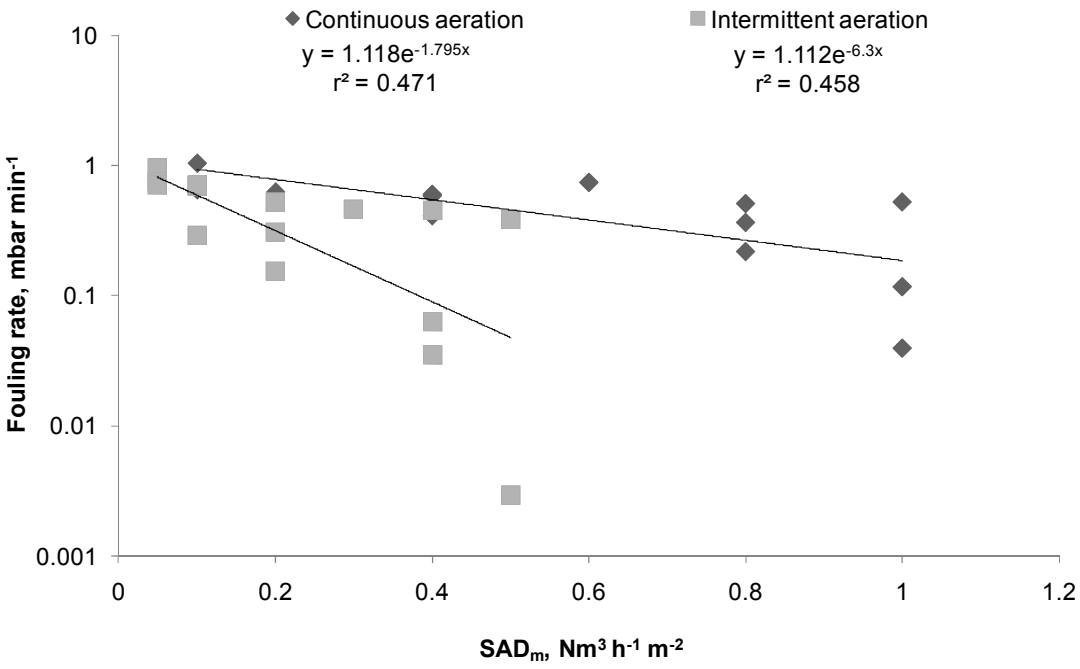

Figure Appendix C.9 Fouling rate *vs* SAD_m for *L1* sidestream module

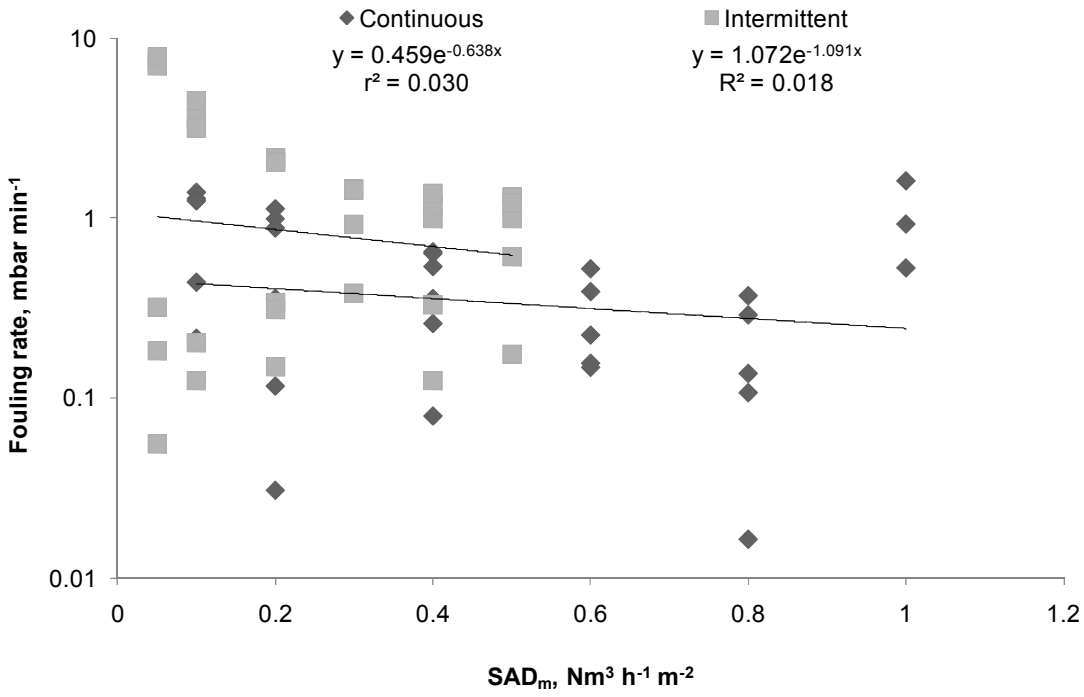

Figure Appendix C.10 Fouling rate *vs* SAD_m for *L2* sidestream module

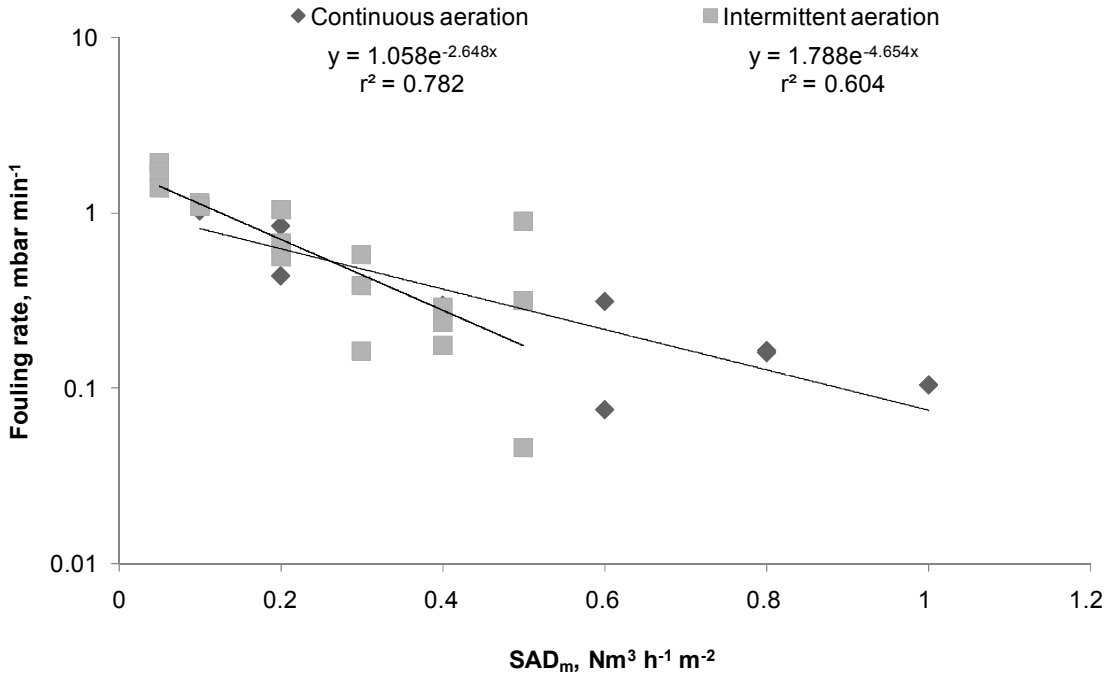

Figure Appendix C.11 Fouling rate *vs* SAD_m for *H1* sidestream module

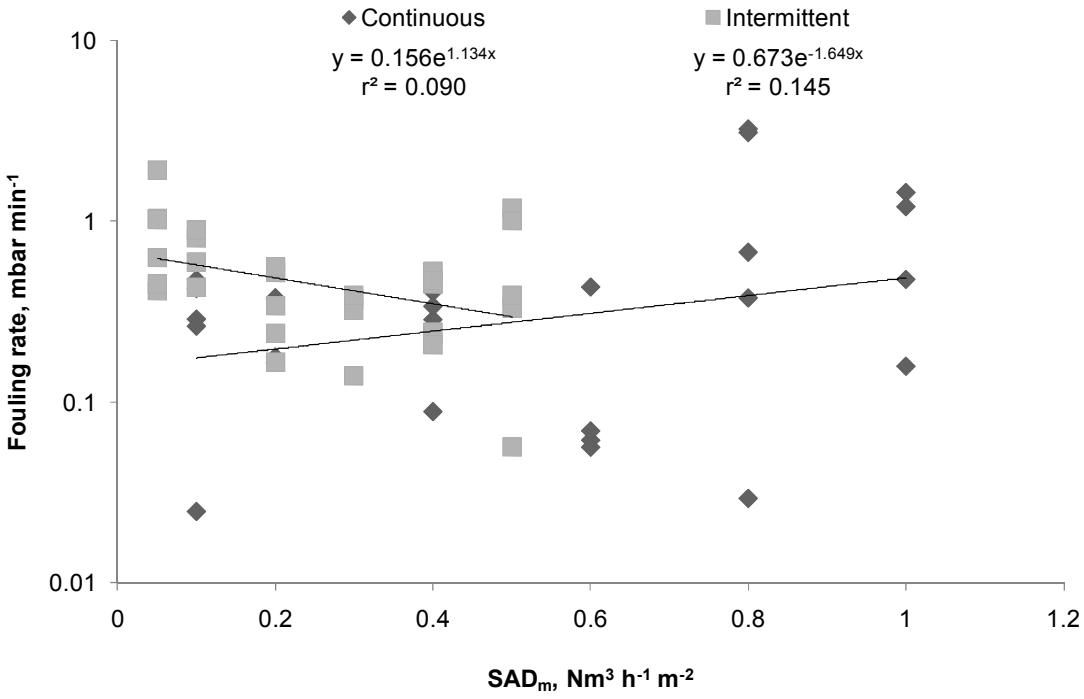

Figure Appendix C.12 Fouling rate *vs* SAD_m for *H2* sidestream module

As would be expected, on average the modules with higher water permeability (*H1* and *H2*) performed slightly better than the modules with lower permeability (*L1* and *L2*).

Table Appendix C.5 Criticality of flux and aeration: summary table

Campaign	4		5	
Modules tested	*L1*	*H1*	*L2*	*H2*
J_c, l m^{-2} h^{-1}				
Continuous	11.90	16.67	17.65	15.72
Intermittent	14.69	15.54	17.10	12.86
$SAD_{m,crit}$, Nm^3 h^{-1} m^{-2}				
Continuous	0.45	0.28	-0.13	1.03
Intermittent	0.13	0.27	0.70	0.18

C.2.2 Sludge upflow tests

Figure Appendix C.13 and Figure Appendix C.14 respectively depict data from the three replicated sludge flow-step tests performed on the *L1* and *H1* sidestream modules with continuous aeration. The results reveal no trend with the upflow velocity, suggesting that for airlift sidestream modules the sludge recirculation can be kept at a minimum. Tests using intermittent aeration were not possible due to the tendency for the sludge to settle during periods without aeration.

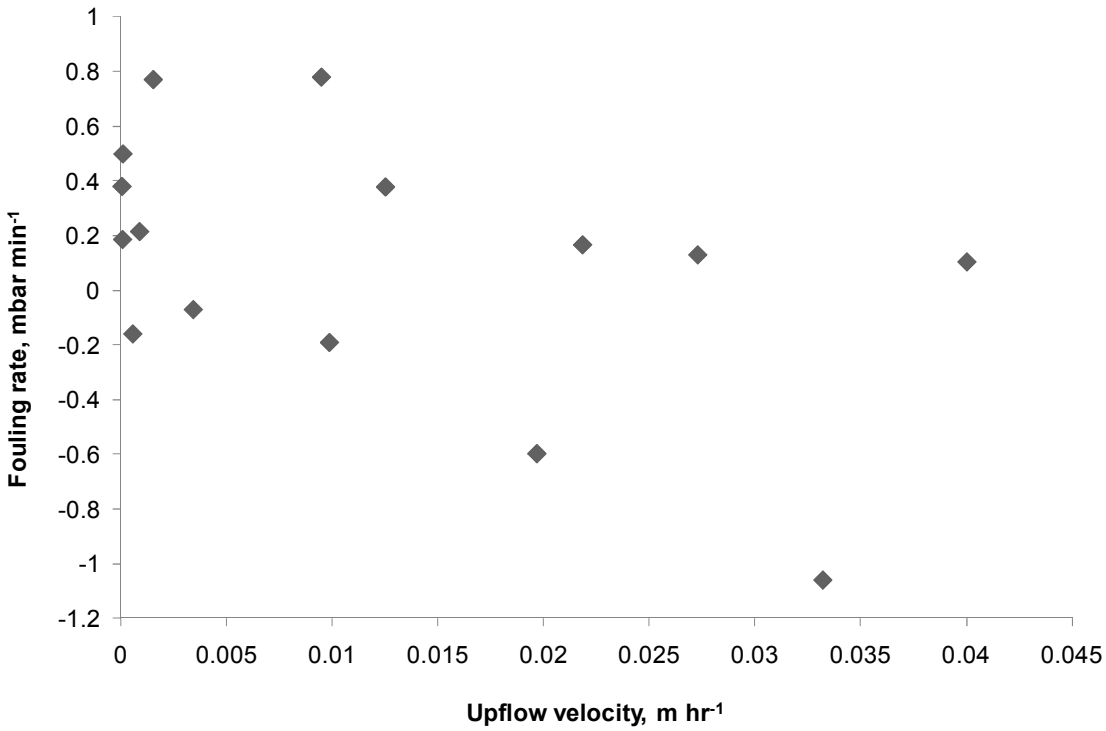

Figure Appendix C.13 Fouling rate *vs* sludge upflow velocity for *L1*

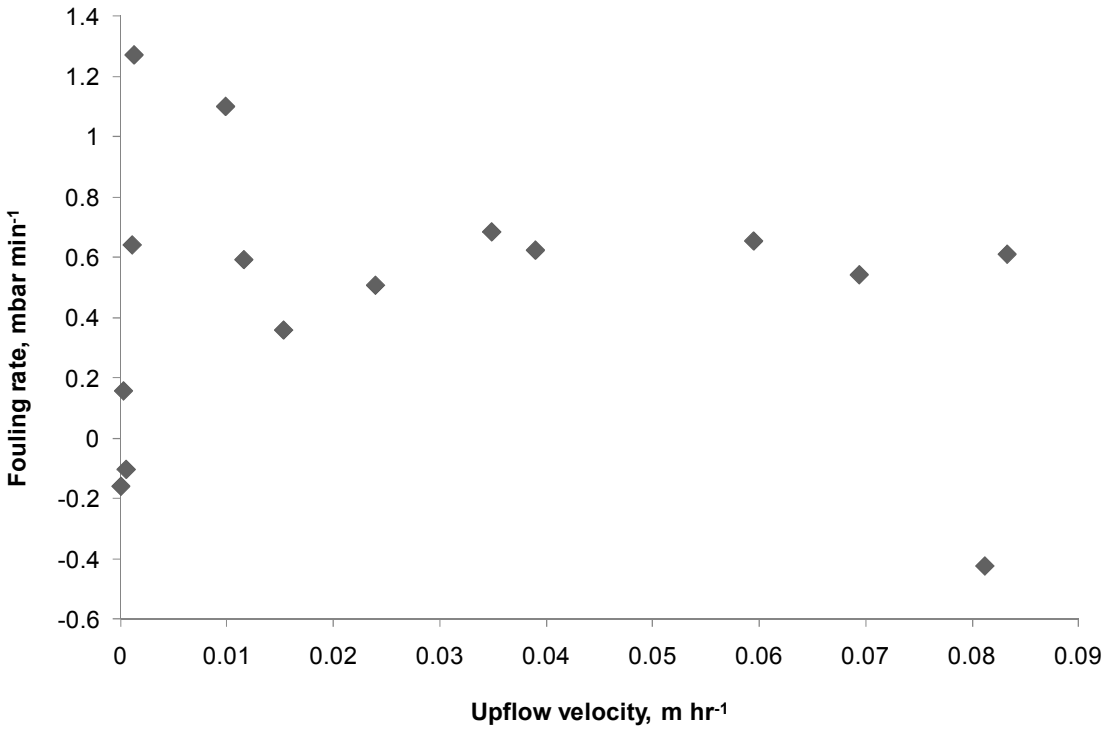

Figure Appendix C.14 Fouling rate *vs* sludge upflow velocity for *H1*

The SAD_m step test was performed under an airlift regime (*i.e.* without sludge pumping) alone on the *L1* and *H1* modules and compared to a test performed under the same conditions with supplementary sludge pumping. A comparison of fouling data obtained for these two operation regime ("pumping" and "airlift") at critical flux values of 12 l m^{-2} h^{-1} for the *L1* and 17 l m^{-2} h^{-1} for the *H1* modules (Figure Appendix C.15; Figure Appendix C.16) reveals airlift to be generally more effective than pumping. Under the airlift regime, no critical SAD_m was observed indicating that the conditions applied were possibility over conservative (Table Appendix C.6). These data appear to confirm that sludge upflow generated by pumping has little impact on fouling, especially when compared with airlift operation. Tests using intermittent aeration were not possible due to the tendency for the sludge to settle during periods without aeration.

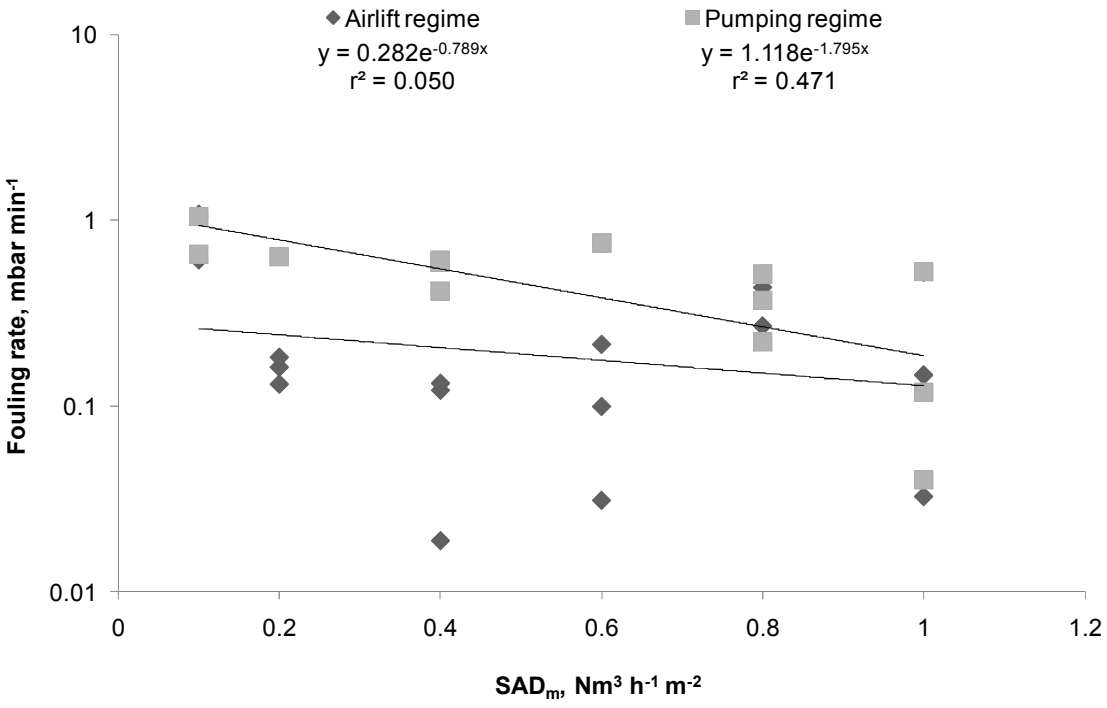

Figure Appendix C.15 Fouling rate *vs* SAD_m for *L1* sidestream module under pumping and airlift regime

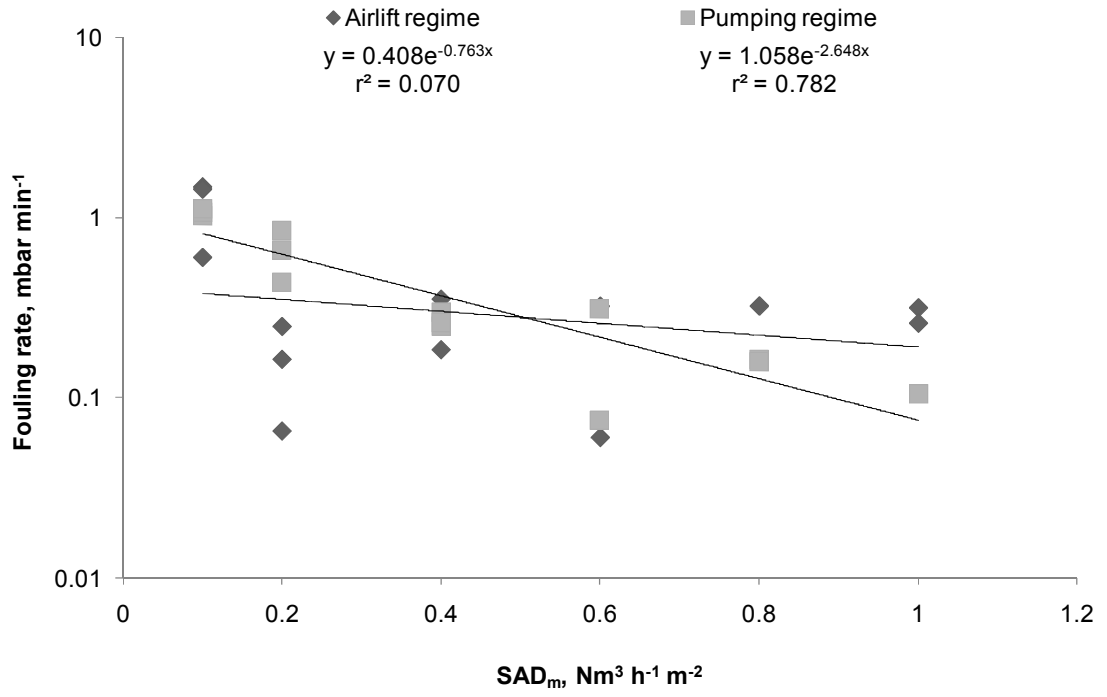

Figure Appendix C.16 Fouling rate *vs* SAD_m for *H1* sidestream module under pumping and airlift regime

Table Appendix C.6 Critical SAD_m

$SAD_{m,crit}$, $Nm^3 h^{-1} m^2$	*L1*	*H1*
Airlift regime	-0.73	-0.27
Pumping regime	0.45	0.28

C.2.3 Statistical analysis

Figure Appendix C.5 to Figure Appendix C.8 reveal the pressure data to be much nosier than for the immersed module (Figure 9.10, Chapter 9). It was established that this was not due to the pressure transducer itself, and also unlikely to be due to the permeate pumping mode since this was the same as that employed for the immersed modules (a peristaltic pump). The scatter in the data may therefore arise from actual the measurement of the pressure, and is not necessarily a facet of the module. Whilst it is possible that this may not be the root cause of the scatter in the fouling rate data (which are based on the average increase in pressure), it seems most likely to be so.

The same statistical analysis as that conducted on the immersed modules was carried out on the sidestream ones (Table Appendix C.7). Although a narrow confident interval was observed for *L2*, overall the confidence intervals are very wide with a deviation varying between 14.5 and 16.7. This is consistent with the low linear regression correlation coefficient, and may relate to the observed aeration pattern producing the pressure transducer data scatter.

Table Appendix C.7 Lower and upper confidence limit for estimated critical flux value (L_1-L_2, interval difference)

Campaign	4		5	
Modules tested	*L1*	*H1*	*L2*	*H2*
Continuous	16.1-32.2 (16.0)	21.9-35.5 (13.6)	21.4-31.1 (9.6)	17.6-32.2 (14.6)
Intermittent	19.3-34.9 (15.6)	20.1-33.9 (13.8)	16.0-30.5 (14.5)	16.2-32.8 (16.7)

C.3 Conclusions

- The criticality data for flux and particularly for aeration were subject to greater variability than that for the immersed modules tested. It was observed that the actual logged pressure data was very noisy (Figure Appendix C.5 to Figure Appendix C.8) compared with those of the immersed module (Figure 9.10, Chapter 9). It was originally thought that this was due to the challenge in reproducing the fabricating modules. The aeration patterns between the modules were visibly different, and it therefore cannot be assumed that the same delivered air flow rate exerted the same degree of scouring from one module to another. No similar issue was encounter with the immersed modules, where the aerator was not integrated with the module. However, it is not necessarily the case that the noisy signal from the pressure sensor is attributable to the module construction, and could be a facet of the monitoring itself.

- The impact of liquid flow on membrane permeability appears insignificant, suggesting that for airlift sidestream modules the sludge recirculation can be kept at a minimum. However the sludge flow rate was controlled using a ball valve which is insufficiently precise; a dedicated sludge flow meter would be beneficial in providing more rigorous control of the sludge flow.

APPENDIX D STATISTICAL ANALYSIS

Ana Santos and Simon J. Judd

Centre for Water Science, Cranfield University, Cranfield, MK43 0AL, UK

D.1 Statistical methodology

For two variables under study, one is known as an *independent variable*, *X*, also called *predictor variable*, and the other variable, *Y*, known as the *dependent* or predicted variable (Arankacami and Rangaswamy, 1995). The relationship between the two variables is expressed as regression, and so linear regression if represented by a straight line. This relationship is given by the following equation:

$$Y_i = a + b_{Y.X} X_i \quad \textbf{(D.1)}$$

In cases where the corresponding value of *X* for a known value of *Y* is required, this is known as *Inverse prediction*, viz.:

$$X_i = \frac{(Y_i - a)}{b_{Y.X}} \quad \textbf{(D.2)}$$

To evaluate how closely the critical flux estimated matches the true value within the whole data acquired, 95% confidence limits were defined: the limits where there is 95% confidence of the values lying within this range of lower (L_1) and upper (L_2) confidence limits. According to Sokal and Rohlf (1995), to estimate *X* from *Y* with 95% confidence limits, a quantity *D* can be defined:

$$D = b_{Y.X}^2 - t_{0.05[n-2]}^2 S_b^2 \quad \textbf{(D.3)}$$

where $b_{Y.X}$ is the intercept of the linear regression, $t_{0.05(n-2)}$ is the *t* value with n-2 degrees of freedom, *n* is the number of samples and S_b the intercept standard error.

Another quantity H,

$$H = \frac{t_{0.05[n-2]}}{D}\sqrt{S_{Y.X}^2\left[D\left(1+\frac{1}{n}\right)+\frac{(Y_i-\bar{Y})^2}{\sum X^2}\right]} \quad \textbf{(D.4)}$$

where $S_{Y.X}$ is the regression standard error, $(Y_i - \bar{Y})$ – the difference between the measured *Y* value corresponding to the estimated value of *X*. *X* then represents the flux value at which the fouling rate, (dTMP/dt) - the *Y* value - exceeds a threshold of 0.5 mbar min^{-1}, both to the power of 2, and $\sum X^2$ the standard deviation for *X* values. The 95% confidence limits are then given by:

$$L_1 = \bar{X} + \frac{b_{Y.X}(Y_i-\bar{Y})}{D} - H \quad \textbf{(D.5)}$$

$$L_2 = \bar{X} + \frac{b_{Y.X}(Y_i-\bar{Y})}{D} + H \quad \textbf{(D.6)}$$

D.2 Analysis

The critical flux data for the immersed modules for campaign 1 to 5 was analysed using the statistical methods described. The estimated lower (L_1) and upper limit (L_2) confidence limit with 95% confidence limits data are summarised in Table Appendix D.1. The confidence limits data reveal:

- The difference between the intervals vary between modules, from ~8 to ~17, with the *B3* test module (with the highest critical flux) having the largest deviation indicating less precision in the critical flux determined, and
- These difference values may be too large for noted differences in critical flux values to be significant

A comparison of the r^2 correlation coefficient values for the entire set of log (dTMP/dt) *vs* flux data set (Table Appendix D.2) compared to those of comparing the critical fluxes obtained using average step values (Table Appendix D.3) and the entire data set (Table Appendix D.2), as expected, in general the r^2 was higher when using average values and the critical fluxes varied less significantly. Also, the absolute values tend to be higher.

Table Appendix D.1 Lower and upper confidence limit for estimated critical flux value (L_1-L_2, (interval difference))

Campaign	1	2	3	4	5
Modules tested	*S2*	*S1, S2, B1, B2*	*S2*	*S2*	*B3*
Continuous			13.1-29.0 (15.9)	13.0-26.7 (13.8)	15.4-31.2 (15.8)
Intermittent	15.0-25.1 (10.1)	*S1*: 9.6-20.0 (10.5) *S2*: 12.9-21.2 (8.2) *B1*: 10.4-22.0 (11.6) *B2*: 8.7-19.4 (10.7)		12.6-25.8 (13.3)	13.5-30.7 (17.2)

Table Appendix D.2 Critical flux (l m^{-2} h^{-1}) tests summary table (entire data set)

Campaign	1	2	3	4	5
Modules tested	*S2*	*S1, S2, B1, B2*	*S2*	*S2*	*B3*
Continuous	-	-	11.1 (r^2=0.78)	14.5 (r^2=0.86)	16.5 (r^2=0.74)
Intermittent	15.6 (r^2=0.95)	*S1*: 6.6 (r^2=0.69)	14.0 (r^2=0.85)	13.0 (r^2=0.94)	15.6 (r^2=0.72)
		S2: 12.0 (r^2=0.38)			
		B1: 8.1 (r^2=0.91)			
		B2: 8.9 (r^2=0.72)			

Table Appendix D.3 Critical flux (l m^{-2} h^{-1}) tests summary table (average step values)

Campaign	1	2	3	4	5
Modules tested	*S2*	*S1, S2, B1, B2*	*S2*	*S2*	*B3*
Continuous	-	-	11.9 (r^2=0.87)	13.0 (r^2=0.92)	17.0 (r^2=0.67)
Intermittent	14.5 (r^2=0.99)	*S1*: 8.4 (r^2=0.82)	13.7 (r^2=0.90)	12.4 (r^2=0.97)	14.3 (r^2=0.78)
		S2: 13.0 (r^2=0.74)			
		B1: 9.0 (r^2=0.93)			
		B2: 6.9 (r^2=0.83)			

It may be concluded that whilst the critical flux values estimated in Table Appendix D.2 and Table Appendix D.3 showed *B3* to have provided the best hydraulic performance, the statistical analyses show greater discrepancy in the data than the difference in critical flux between module types. Against this, the *B3* module appears to provide the highest critical flux regardless of the statistical processing approach.

D.3 References

Arankacami, I. and R. Rangaswamy, R. (1995), *Textbook of agricultural statistics*, New Age International, India.

Sokal, R. R. and F. J. Rohlf. (1995), *Biometry: the principles and practice of statistics in biological research*, 3rd ed., W. H. Freeman and Co., New York.